

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-119204

(43)Date of publication of application : 23.04.2003

(51)Int.Cl.

C08F 2/26

C08F 14/18

C08F 16/24

(21)Application number : 2001-309905

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(22)Date of filing : 05.10.2001

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(54) METHOD FOR MANUFACTURING FLUORINE-CONTAINING POLYMER LATEX

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for manufacturing a fluorine-containing polymer latex for furnishing a fluorine-containing polymeric material having excellent powder properties and mechanical properties when molded that are comparable with those of the conventional materials.

SOLUTION: This fluorine-containing polymer latex is manufactured by subjecting to emulsion polymerization in an aqueous medium, a single fluorine-containing olefin, or a fluorine-containing olefin and another monomer, in the presence of at least one type of fluorine-containing surfactant represented by formula (I): $Rf1O(CFX-CF2O)_p-CFX-COOM$, formula (II): $Rf2OCF2(CH2)_nO(CFX-CF2O)_p-CFX-COOM$, formula (III): $M1OCO(CF2)_mCOOM2$, or formula (IV): $Rf3(CH2)_nOCO-CH(SO3M)-CH2-COO(CH2)_n'Rf3'$, (wherein $Rf1$ is a 1-5C perfluoroalkyl group; $Rf2$ is a 2-3C alkyl group other than a perfluoroalkyl group that contains one or more fluorine atom; $Rf3$ and $Rf3'$ are, the same or different, a 1-4C alkyl group having one or more fluorine atom; and X is a fluorine atom, a chlorine atom, or a 1-4C perfluoroalkyl group).

LEGAL STATUS

[Date of request for examination] 24.08.2004

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

(Claim 1) (Formula I): $R(O(CFX-CF_2O)_p-CFX-COOM)$ (among a formula) $R11$ — perfluoroalkyl radical [of carbon numbers 1–5]; X — a fluorine atom — integer; M of 0–5 perfluoroalkyl radical of a chlorine atom or carbon numbers 1–4 hydrogen atom, the fluorine-containing surfactant with which it is expressed by ammonium, the alkali-metal atom, or the alkaline-earth-metal atom (I), Formula (II): $R12(CF_3CH_2)_n(O(CFX-CF_2O)_p-CFX-COOM)$ (among a formula) alkyl group [of the carbon numbers 2 or 3 whose $R2$ is not or more 1 hidden perfluoro onto a fluorine atom]; n — integer [of 1–3]; X — a fluorine atom — integer; M of 0–5 perfluoroalkyl radical of a chlorine atom or carbon numbers 1–4 hydrogen atom, the fluorine-containing surfactant with which it is expressed by ammonium, the alkali-metal atom, or the alkaline-earth-metal atom (II), Formula (III): $M1OCO(CF_2)mCOOM2$ (as for m , integer; M of 2–4 and $M2$ are a hydrogen atom, ammonium, an alkali-metal atom, or an alkaline-earth-metal atom among a formula) even when it is the same — differing — — — — the fluorine-containing surfactant (III) with which it is expressed — Or formula (IV): $R13(CH_2)_nOCO-CH(SO_3M)-CH_2-COOCH_2R'3$ (where $R13$ and $R'3$ are the alkyl groups of the carbon numbers 1–4 containing one or more fluorine atoms among a formula) the same; and n which may differ but becomes independent. Integer; M of 1–3 A hydrogen atom, Under at least one sort of a fluorine-containing surfactant (IV) of existences expressed by ammonium, the alkali-metal atom, or the alkaline-earth-metal atom, in an aqueous medium The manufacture approach of the fluorine polymer latex which is fluorine-containing olefin independent or is characterized by carrying out the emulsion polymerization of a fluorine-containing olefin and other monomers.

[illegible]

(Claim 3) The manufacture approach according to claim 1 that said fluorine-containing surfactant (II) is $\text{H}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{OCF}(\text{CF}_3)\text{COONH}_4$.

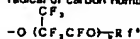
[Claim 4] The manufacture approach according to claim 1 that said fluorine-containing surfactant (III) is $\text{H}_4\text{NOCO}(\text{CF}_2\text{CF}_2)_2\text{COONH}_4$.

[Claim 5] The manufacture of process according to claim 1 that said fluorine-containing surfactant (IV) is $\text{H}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{CH}_2\text{COOCH}(\text{SO}_3\text{NH}_4)$ $\text{CH}_2\text{COOCH}_2(\text{CF}_2\text{CF}_2)_2\text{H}$ or $\text{H}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{CH}_2\text{COOCH}(\text{SO}_3\text{Na})\text{CH}_2\text{COOCH}_2(\text{CF}_2\text{CF}_2)_2\text{H}$.

[Claim 6] said fluorine-containing olefin — formula (1): — [Formula 1]



For the inside of [type, and Y1, F, Cl, H, or CF3; Y2 are F, Cl, H, Rf5 (Rf5 is the perfluoroalkyl radical of carbon numbers 1-10), or [Formula 2].



The monomer shown by], or a formula (2) (Rf6 is the perfluoroalkyl radical of carbon numbers 1-6, and b is the integer of 0, or 1-5) [Formula 3]



[—the manufacture approach according to claim 1 to 5 that the inside of a formula and Z1 are one sort of the monomer perfluoroalkyl radical; Z2 of the alkyl group of F, H, and carbon numbers 1-6 or carbon numbers 1-10 are indicated to be by the alkyl group of H, Cl, and carbon numbers 1-6, or -(CF2)^d-Z3(d is integer of 1-10 and Z3 is F or H)], or two sorts or more.

[Claim 7] The manufacture approach according to claim 6 that said fluorine-containing olefin is a par halo olefin Y1 and whose Y2 are either F, Cl or Rf5 in a formula (1).

(Claim 8) The manufacture approach according to claim 7 that said per halo olefin is tetrafluoroethylene, perfluoro (alkyl vinyl ether), hexafluoropropylene, or chlorotrifluoroethylene.

[Claim 9] The manufacture approach according to claim 8 that said fluorine-containing olefin is vinylidene fluoride each of Z1 and whose Z2 is F in a formula (2).

[Claim 10] said — others — the manufacture approach according to claim 1 to 9 that a monomer is one sort of the ethylenic unsaturated monomer of a non-fluorine system, or two sorts or more.

(Claim 11) The manufacture approach according to claim 1 to 7 that the fluorine polymer obtained is a par halo polymer.

[Claim 12] or [that said par halo polymer has denaturalized] — or the manufacture approach according to claim 11 which is the polytetrafluoroethylene which is not carried out, a tetrafluoroethylene-hexafluoropropylene copolymer, a tetrafluoroethylene-perfluoro (alkyl vinyl ether) copolymer, or polychlorotrifluoroethylene resin.

[Claim 13] The manufacture approach according to claim 1 to 7 that the fluorine polymer obtained is a non-par halo polymer.

(Claim 14) Said non-par halo polymer The homopolymer of vinylidene fluoride, trifluoro ethylene, or vinyl fluoride, or these two or more sorts of copolymer, tetrafluoroethylene, Perfluoro (alkyl vinyl ether), hexafluoropropylene, or chlorotrifluoroethylene and vinylidene fluoride, Two or more sorts of copolymer, or tetrafluoroethylenes of trifluoro ethylene and vinyl fluoride, 2, 3, 3, 4 and 5, 5-heptafluoro-1-pentene or 3 and 3, and a 3-trifluoro-2-(trifluoromethyl)-1-propene, Perfluoro (alkyl vinyl ether), hexafluoropropylene, Chlorotrifluoroethylene, and vinylidene fluoride, trifluoro ethylene, One sort or two sorts or more, and ethylene of vinyl fluoride, 2, 3, 3, 4, 4 and 5, 5-heptafluoro-1-pentene or 3 and 3, and a 3-trifluoro-2-(trifluoromethyl)-1-propene, The manufacture approach according to claim 13 which are one sort of a propylene, vinyl ether, vinyl ester, or acrylate, or two sorts or more of copolymers.

[Claim 15] The manufacture approach according to claim 1 to 14 which adds at least one sort of a fluorine-containing surfactant according to claim 1 to 5 in 0.001 – 15.0% of the weight of an amount to an aqueous medium at the time of polymerization initiation, and starts an emulsion polymerization.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the fluorine polymer latex which carries out the emulsion polymerization of the fluorine-containing olefin in an aqueous medium to the bottom of existence of a specific fluorine-containing surfactant.

[0002]

[Description of the Prior Art] When carrying out an emulsion polymerization in aqueous dispersion liquid by making a fluorine-containing olefin into a monomer and manufacturing a fluorine polymer latex conventionally, it is indispensable to make a surfactant (emulsifier) exist in a polymerization system, and various kinds of surfactants are proposed and used.

[0003] It is known that such a surfactant will affect the mechanical property, the various properties, for example, fine-particles property, of the fluorine polymer obtained, of mold goods (JP.52-52984A, JP.57-184199A, JP.61-223007A, JP.7-292008A, JP.11-246807A, JP.11-512133A, JP.2001-84304A, U.S. Pat. No. 3,391,099 specification, etc.).

[0004] Moreover, even if it calls it an emulsifier, as for the compound with the concern which affects an environment and an ecosystem, it is desirable not to use it as much as possible.

[0005]

[Problem(s) to be Solved by the Invention] This invention performs the emulsion polymerization of a fluorine-containing olefin using a specific fluorine-containing surfactant with affecting [little] an environment and an ecosystem, and aims at offering the approach of manufacturing the fluorine polymer latex which gives the fluorine polymer ingredient which is equal in a fine-particles property or the mechanical property of mold goods compared with the polymer obtained using a general-purpose emulsifier.

[0006]

[Means for Solving the Problem] That is, this invention is (Formula I): $\text{Rf1O}(\text{CFX}-\text{CF2O})_p\text{-CFX-COOM}$ (among a formula), Rf1 — perfluoroalkyl radical of carbon numbers 1-5; — X — a fluorine atom — Integer: M of 0-5 perfluoroalkyl radical of a chlorine atom or carbon numbers 1-4 a hydrogen atom. The fluorine-containing surfactant with which it is expressed by ammonium, the alkali-metal atom, or the alkaline-earth-metal atom (II), Formula (II): $\text{Rf2CF2}(\text{CH2})_n\text{O}(\text{CFX}-\text{CF2O})_p\text{-CFX-COOM}$ (among a formula) alkyl group [of the carbon numbers 2 or 3 whose Rf2 is not or more 1 hidden perfluoro about a fluorine atom]; — n — integer of 1-3; — X — a fluorine atom — Integer: M of 0-5 perfluoroalkyl radical of a chlorine atom or carbon numbers 1-4 a hydrogen atom. The fluorine-containing surfactant with which it is expressed by ammonium, the alkali-metal atom, or the alkaline-earth-metal atom (II), Formula (III): $\text{M1OCO}(\text{CF2})_m\text{COOM2}$ (as for m, integer: M1 of 2-4 and M2 are a hydrogen atom, ammonium, an alkali-metal atom, or an alkaline-earth-metal atom among a formula) even when it is the same — differing — the fluorine-containing surfactant (III) with which it is expressed — Or formula (IV): $\text{Rf3}(\text{CH2})_n\text{OCO-CH}(\text{SO3M})\text{-CH2-COO}(\text{CH2})_n\text{Rf3}$ (Rf3 and Rf3' are the alkyl groups of the carbon numbers 1-4 containing one or more fluorine atoms among a formula) The same n' which may differ but becomes independent. Integer: M of 1-3 a hydrogen atom. Under at least one sort of a fluorine-containing surfactant (IV) of existences expressed by

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COOM (Integer: M of 0-5 is [the inside of a formula, and Rf1 / perfluoroalkyl radical: X of carbon numbers 1-5] a hydrogen atom, ammonium, an alkali-metal atom, or an alkaline-earth-metal atom for perfluoroalkyl radical: p of a fluorine atom, a chlorine atom, or carbon numbers 1-4) (I).

[0021] This fluorine-containing surfactant (I) has the description in the point of lowering the surface tension of a polymerization system by low concentration, and when p is a time of especially the inside Rf1 of a formula being [p] 1 or 2 in the perfluoroalkyl radical of carbon numbers 1 or 2 and Rf1 is 0 in the perfluoroalkyl radical of a carbon number 5, the outstanding surface tension fall ability is demonstrated. Moreover, when M is ammonium, it is advantageous at the point that it is easily removable from a generation polymer with heat-treatment.

[0022] As a desirable example of said fluorine-containing surfactant (I) $\text{CF3OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{COONH4}$, $\text{CF3OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{COONH4}$, $\text{CF3OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{COONH4}$, $\text{CF3OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{COONH4}$, $\text{CF3OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{COONH4}$ (CF3) Or one sort of $\text{CF3CF2CF2CF2CF2OCF}(\text{CF3})\text{COONH4}$ or two sorts or more are raised. From the point of excelling in the capacity to distribute especially a fluorine system monomer $\text{CF3OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{COONH4}$, $\text{CF3OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{COONH4}$, $\text{CF3OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{COONH4}$, $\text{CF3OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{COONH4}$, or $\text{CF3OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{CF2OCF}(\text{CF3})\text{COONH4}$ is desirable.

[0023] (II) Formula (II): $\text{Rf2CF2}(\text{CH2})_n\text{O}(\text{CFX}-\text{CF2O})_p\text{-CFX-COOM}$ (among a formula) alkyl group [of the carbon numbers 2 or 3 whose Rf2 is not or more 1 hidden perfluoro about a fluorine atom]; — n — integer of 1-3; — X — a fluorine atom — For integer: M of 0-5, perfluoroalkyl radical: p of carbon numbers 1-4 is a chlorine atom or a fluorine-containing surfactant with which it is expressed by the hydrogen atom, ammonium, the alkali-metal atom, or the alkaline-earth-metal atom (II).

[0024] This fluorine-containing surfactant (II) has the description in the point of excelling in the capacity to distribute the fluorine system monomer containing a hydrogen atom, and when n is 1 in the fluoro alkyl group in which especially the inside Rf2 of a formula contains one hydrogen atom, the improvement effectiveness in dispersibility of outstanding vinylidene fluoride or trifluoro ethylene is demonstrated.

[0025] The point which $\text{H}(\text{CF2CF2})_2\text{CH2OCF}(\text{CF3})\text{COOH}$ or $\text{H}(\text{CF2CF2})_2\text{CH2OCF}(\text{CF3})\text{COONH4}$ etc. is raised, and can be especially removed from a generation polymer easily by heat-treatment as an example of said fluorine-containing surfactant (II) to $\text{H}(\text{CF2CF2})_2\text{CH2OCF}(\text{CF3})\text{COONH4}$ is desirable.

[0026] (III) formula (III): — the fluorine-containing surfactant (III) expressed with $\text{M1OCO}(\text{CF2})_m\text{COOM2}$ (it may differ among the formula even if integer: M1 [of 2-4] and M2 are a hydrogen atom, ammonium, an alkali-metal atom, or an alkaline-earth-metal atom and m is the same).

[0027] When both M1 and M2 are ammonium, heat-treatment can remove especially this fluorine-containing surfactant from a generation polymer easily.

[0028] The point which $\text{H4NOCO}(\text{CF2CF2})_2\text{COONH4}$, $\text{NaOCO}(\text{CF2CF2})_2\text{COONa}$, $\text{KOCO}(\text{CF2CF2})_2\text{COOK}$, etc. are raised, and can be especially removed from a generation polymer easily by heat-treatment as an example of said fluorine-containing surfactant (III) to $\text{H4NOCO}(\text{CF2CF2})_2\text{COONH4}$ is desirable.

[0029] (IV) Formula (IV): $\text{Rf3}(\text{CH2})_n\text{OCO-CH}(\text{SO3M})\text{-CH2-COO}(\text{CH2})_n\text{Rf3}$ (Rf3 and Rf3' are the alkyl groups of the carbon numbers 1-4 containing one or more fluorine atoms among a formula) For integer: M of 1-3, same n' which may differ but same n' are a fluorine-containing surfactant with which it is expressed by the hydrogen atom, ammonium, the alkali-metal atom, or the alkaline-earth-metal atom independently (IV).

[0030] This fluorine-containing surfactant has the description in the stability of a micell, and the micell stability in which Rf3' and n' were excellent with the same time is demonstrated especially the inside Rf3 of a formula. Moreover, when M is ammonium, heat-treatment can remove from a generation polymer easily.

[0031] As an example of said fluorine-containing surfactant (IV) $\text{H}(\text{CF2CF2})_2\text{CH2OCOCOH}(\text{SO3Na})\text{CH2COOCCH2}(\text{CF2CF2})_2\text{H}$, $\text{H}(\text{CF2CF2})_2\text{CH2OCOCOH}(\text{SO3Na})\text{CH2COOCCH2}(\text{CF2CF2})_2\text{H}$, $\text{H}(\text{CF2CF2})_2\text{CH2OCOCOH}(\text{SO3K})\text{CH2COOCCH2}(\text{CF2CF2})_2\text{H}$, etc. are raised. The point that it is easily removable from a generation polymer especially with heat-treatment to $\text{H}(\text{CF2CF2})_2\text{CH2OCOCOH}(\text{SO3Na})\text{CH2COOCCH2}(\text{CF2CF2})_2\text{H}$ is desirable.

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ammonium, the alkali-metal atom, or the alkaline-earth-metal atom, in an aqueous medium it is related with the manufacture approach of the fluorine polymer latex which is fluorine-containing olefin independent or is characterized by carrying out the emulsion polymerization of a fluorine-containing olefin and other monomers.

[0007] As a fluorine-containing olefin with which a polymerization is presented, it is formula (1):

[0008]



[0009] For the inside of [type, and Y1, F, Cl, H, or CF3; Y2 are F, Cl, H, Rf5 (Rf5 is the perfluoroalkyl radical of carbon numbers 1-10), or [0010].

[Formula 5]



[0011] (Rf5 is the perfluoroalkyl radical of carbon numbers 1-6, and b is the integer of 0, or 1-5) The monomer shown by, or formula (2): [0012]

[Formula 6]



[0013] [— as for Z1, one sort of the monomer perfluoroalkyl radical: Z2 of the alkyl group of F, H, and carbon numbers 1-6 or carbon numbers 1-10 are indicated to be by the alkyl group of H, Cl, and carbon numbers 1-6 or —(CF2) d—Z3 (d is integer of 1-10 and Z3 is F or H)], or two sorts or more are raised among a formula.

[0014] These may be the par halo olefin Y1 and whose Y2 are either F, Cl or Rf5, i.e., tetrafluoroethylene, perfluoro (alkyl vinyl ether), hexafluoropropylene, or chlorotrifluoroethylene in a formula (1), and may be vinylidene fluoride each of Z1 and whose Z2 is F in a formula (2).

[0015] Moreover, as a monomer besides the above, one sort of the ethylenic unsaturated monomer of a non-fluorine system or two sorts or more are raised.

[0016] Consequently, the fluorine polymer obtained turns into a par halo polymer or a non-par halo polymer.

[0017] Whether it has denaturalized as a par halo polymer Or the polytetrafluoroethylene which is not carried out. A tetrafluoroethylene-hexafluoropropylene copolymer, a tetrafluoroethylene-perfluoro (alkyl vinyl ether) copolymer, or polychlorotrifluoroethylene resin is raised preferably. As a non-par halo polymer, the homopolymer of vinylidene fluoride, trifluoro ethylene, or vinyl fluoride, or these two or more sorts of copolymer; tetrafluoroethylenes, Perfluoro (alkyl vinyl ether), hexafluoropropylene, or chlorotrifluoroethylene and vinylidene fluoride, two or more sorts of copolymer; or tetrafluoroethylenes of trifluoro ethylene and vinyl fluoride, 2, 3, 3, 4, 4 and 5, 5-heptafluoro-1-pentene or 3 and 3, and a 3-trifluoro-2-(trifluoromethyl)-1-propene, Perfluoro (alkyl vinyl ether), hexafluoropropylene, Chlorotrifluoroethylene, and vinylidene fluoride, trifluoro ethylene, One sort or two sorts or more, and ethylene of vinyl fluoride, 2, 3, 3, 4, 4 and 5, 5-heptafluoro-1-pentene or 3 and 3, and a 3-trifluoro-2-(trifluoromethyl)-1-propene. One sort of a propylene, vinyl ether, or acrylate or two sorts or more of copolymers are raised preferably.

[0018] In this invention, it is desirable from the various physical properties of the fluorine polymer from which adding at least one sort of said specific fluorine-containing surfactant in 0.001 — 15.0% of the weight of an amount to an aqueous medium at the time of polymerization initiation, and starting an emulsion polymerization is obtained becoming good.

[0019]

[Embodiment of the Invention] This invention has the description in the point which uses a specific fluorine-containing surfactant. Hereafter, a field size activator is explained.

[0020] (I) Fluorine-containing surfactant expressed with (Formula I): $\text{Rf1O}(\text{CFX}-\text{CF2O})_p\text{-CFX-}$

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$2\text{CH2COCH}(\text{SO3NH4})\text{CH2COOCH2}(\text{CF2CF2})_2\text{H}$ are desirable.

[0032] In addition, as long as it requires in addition to this specific fluorine-containing surfactant, perfluoro octanoic acid ammonium, perfluoro nonoic acid ammonium, etc. may be used together.

[0033] Moreover, the surfactant of the anion system of a hydrocarbon system, a cation system, the Nonion system, and a betaine system may be used together.

[0034] Concurrent use of the surface active agent of a hydrocarbon system has the example of a not general thing in manufacture of perfluoro polymer: including polytetrafluoroethylene (PTFE), JP.61-52842.B, JP.48-34837.B, etc. have a publication that the particle diameter of a polymer can be made small by adding 1-5 ppm of polyethylene glycol octyl phenyl ether of a nonionic surfactant with the propylene oxide as a hydrophobic group, perfluoro carboxylate, and a hydrocarbon dispersant, for example, the ethylene oxide as a hydrophilic radical, to an aqueous medium in the case of the emulsion polymerization of PTFE.

[0035] On the other hand, in using the monomer containing hydrogen atoms, such as vinylidene fluoride, as one of the components, it uses the surfactant of a hydrocarbon system together in many cases. For example, the aqueous dispersion liquid of a vinylidene fluoride (VdF) system polymer can be manufactured by carrying out the emulsion polymerization of the monomer mixture which contains a VdF monomer or VdF to water under coexistence with said fluorochemical surfactant below 1 mass %, and the Nonion system non-fluorochemical surfactant of a minute amount.

[0036] Although use of a lot of [particle diameter / in order to prepare the aqueous dispersion liquid whose solid content concentration is 30 to 50 mass % including a VdF system polymer 200nm or less / usually] fluorochemical surfactants is needed, the amount of the fluorochemical surfactant used can be held down to small quantity below 1 mass % by adding an Nonion system non-fluorochemical surfactant in a minute amount. That is, addition of an Nonion system non-fluorochemical surfactant can attain the small particle diameter of 200nm or less.

[0037] As an Nonion system non-fluorochemical surfactant, polyoxyethylene alkyl ether, polyoxyethylene alkyl phenyl ether, polyoxyethylene alkyl ester, sorbitan alkyl ester, polyoxyethylene sorbitan alkyl ester, glycerol ester, the derivative of those, etc. are raised.

[0038] As a thing of polyoxyethylene alkyl ether, more specifically The polyoxyethylene lauryl ether, The polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, The polyoxyethylene oleyl ether, polyoxyethylenebehenyl ether, etc. are raised. As a thing of polyoxyethylene alkyl phenyl ether, the polyoxyethylene nonylphenyl ether, Polyoxystyrene octyl phenyl ether, etc. are raised. As a thing of polyoxyethylene alkyl ester A mono-lauric-acid polyoxyethylene glycol, A mono-oleic acid polyethylene glycol, a monostearin acid polyethylene glycol, etc. are raised. As a thing of sorbitan alkyl ester, mono-lauric-acid polyoxyethylene sorbitan, Mono-palmitic-acid polyoxyethylene sorbitan, mono-oleic acid polyoxyethylene sorbitan, etc. are raised. As a thing of polyoxyethylene sorbitan alkyl ester, mono-lauric-acid polyoxyethylene sorbitan, Mono-palmitic-acid polyoxyethylene sorbitan, monostearin acid polyoxyethylene sorbitan, etc. are raised, and mono-myristic-acid glyceryl, monostearin acid glyceryl, mono-oleic acid glyceryl, etc. are raised as a thing of glycerol ester. Moreover, as these derivatives, polyoxyethylene alkylamine, a polyoxyethylene alkylphenyl-formaldehyde condensate, polyoxyethylene-alkyl-ether phosphate, etc. are raised. It is polyoxyethylene alkyl ether and polyoxyethylene alkyl ester, an HLB value is the thing of 10-18, and, specifically, especially a desirable thing is the polyoxyethylene lauryl ether (EO:5-20). The monostearin acid polyethylene glycol (EO:10-55) and mono-oleic acid polyethylene glycol (EO:8-10) EO indicates the number of ethylene oxide units to be raised.

[0039] This invention — setting — the amount of the Nonion system non-fluorochemical surfactant used — water — receiving — 0.001 to 0.1 mass % — it is 0.01 to 0.05 mass % preferably. If [than 0.1 mass %] more, the fall of the rate of polymerization by chain transfer, a reaction halt, etc. happen and are not practical. Moreover, the effectiveness of particle diameter micinizing is hardly seen under by 0.001 mass %.

[0040] These specific fluorine-containing surfactants may be used independently, may be used together, or may be used together with the fluorine-containing surfactant of further others, and/or a non-fluorochemical surfactant. That to which other surfactants in the case of using together do not affect an environment and an ecosystem should be selected.

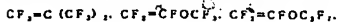
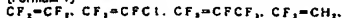
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[0041] As a fluorine-containing olefin which is the monomer which carries out a polymerization, the monomer shown by said formula (1) or formula (2) is raised with the manufacture approach of this invention, and a polymerization is presented with 1 of sorts of these, and two sorts or more.

[0042] As an example of the monomer shown by the formula (1), it is [0043].

[Formula 7]



[0044] *** is raised preferably.

[0045] Perfluoroolefins and chlorotrifluoroethylenes (CTFE), such as par halo olefins (TFE), for example, tetrafluoroethylene, hexafluoropropylene (HFP), and perfluoro (alkyl vinyl ether), are especially desirable.

[0046] As an example of the monomer shown by the formula (2), $CH_2=CHF$, $CH_2=CF_2$, $CH_2=CF_2$, $CH_2=CHCF_3$, $CH_2=CHCF_3$, $CH_2=CHCF_3$, $CH_2=CHCF_3$, etc. can be raised preferably, for example. The vinylidene fluoride especially shown by $CH_2=CF_2$ is desirable.

[0047] In this invention, these fluorine-containing olefins can be homopolymerized, or fluorine-containing olefins can be copolymerized, and it can copolymerize with the ethylenic unsaturated monomer of a non-fluorine system further.

[0048] As an ethylene nature partial saturation non-fluorine monomer, for example Ethylene, a propylene, Isobutene and a formula: $CH_2=CH-O-C(=O)-R^7$ (among a formula) R^7 The aliphatic series radical of carbon numbers 1-17, the aliphatic radical of carbon numbers 3-17, the fluoro alkyl group of carbon numbers 1-20. The alkyl vinyl ether or vinyl ester shown is raised. $e^- - 0$ or $1 - 1$ is — as an example For example, the methyl vinyl ether, ethyl vinyl ether, n-propyl vinyl ether, isopropyl vinyl ether, n-butyl vinyl ether, isobutyl vinyl ether, Cyclohexyl vinyl ether, 2 and 2, 2-trifluoroethyl vinyl ether, 2, 2, 3, 3 and 3-tetrafluoro propyl vinyl ether, 2, 2, 3, 3, 3-pentafluoro propyl vinyl ether, Acetic acid vinyl ester, propionic acid vinyl ester, butanoic acid vinyl ester, pivalic acid vinyl ester, BASA tic acid vinyl ester, cyclohexane-carboxylic acid vinyl ester, etc. are raised.

[0049] Furthermore, it is formula: [0050].

[Formula 8]



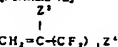
[0051] the inside of a formula, and Z^1 — H, Cl, F, CH_3 , and CF_3 , R^8 — H, Cl, and F — The compound expressed with the aliphatic series radical of carbon numbers 1-17, the aliphatic radical of carbon numbers 3-17, or the fluoro alkyl group of carbon numbers 1-20 is raised. As an example isobutyl acrylate, methyl acrylate, ethyl methacrylate, 2, 2, 3, 3, 3 and 3-pentafluoro propyl-alpha-fluoro acrylate, 2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, 7 and 7-dodeca fluoro penta-alpha-trifluoromethyl acrylate, Cyclohexyl acrylate, 2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, 7, 8, 8, 9, 9, 10, 10, 11, 12, 12, 13, 13, 14, 14, 15 and 15, and 15-nonacos fluoro penta-decyl acrylate, Octyl-alpha-chloro acrylate, octadecyl acrylate, etc. are raised.

[0052] Moreover, the compound shown by formula: $CH_2=CHCH_2 Z^2$ (Z^2 shows the alkoxy group of a chlorine atom or carbon numbers 1-8 among a formula) can also be used, and an allyl

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[Formula 12]

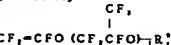


[0068] The hexafluoro isobutylene as the above with (same) Z^3 , Z^4 , and i.e. is desirable.

[0069] One of the copolymers of the shape of an elastomer which uses TFE as a principal component is a copolymer with which TFE consists of 40-70-mol % and 30-60 mol % of propylenes] Z^1 moreover — these — others — a copolymerizable component, for example, VdF and HFP, CTFE, and perfluoro vinyl ether — less than [40 mol %] — it can also contain.

[0070] Another elastomer-like polymer is a polymer which consists of TFE and perfluoro vinyl ether, and is 40-85 mol % and type: [0071]. [of TFE(s)]

[Formula 13]



[0072] Perfluoroalkyl radical of carbon numbers 1-8 is shown by integer of 0, or 1-5, and (type Naka and R9 are perfluoro vinyl ether 15 - 50-mol % of a polymer.

[0073] The 2nd group of a desirable fluorine polymer which manufactures by the manufacture approach of this invention is a polymer which uses VdF as a principal component.

[0074] namely, the copolymer obtained by using VdF as an indispensable component and copolymerizing other monomers if needed further — it is — VdF — more than 40 mol % — it is the fluorine polymer to contain.

[0075] In this VdF system polymer, TFE, CTFE, HFP, hexafluoro isobutene, and perfluoro vinyl ether are desirable examples as other copolymerizable monomers.

[0076] As an example of the fluorine polymer which uses VdF as a principal component, the homopolymer (PvDF) of VdF, the copolymer of VdF and TFE, the copolymer of VdF and HFP, the copolymer of VdF and TFE and HFP, the copolymer of VdF, TFE, and CTFE, the copolymer of VdF, TFE, and $CF_3 OCF_2 CF_2$, etc. are raised preferably.

[0077] Moreover, these fluorine polymers that use VdF as a principal component can be used as the polymer of the shape of the shape of resin, and an elastomer by choosing various other existence, classes, and presentation ratios of a monomer component to copolymerize.

[0078] As an example of the VdF system polymer of the shape of desirable resin, a VdF/TFE (50 - 99 / 1-50-mol ratio (%)) copolymer, a VdF/TFE/HFP (% 45 - 99/0 - 45 / 1-10-mol ratio) copolymer, a VdF/TFE/CTFE (% 50 - 99/0 - 30 / 1-20-mol ratio) copolymer, VdF/TFE/HFP (% 45 - 99/0 - 45 / 1-15-mol ratio), etc. are raised also in it.

[0079] Moreover, as an example of the presentation range which becomes elastomer-like, 40-85-mol % and TFE are raised for VdF, and 15-50-mol % of a copolymer is preferably raised with a VdF system copolymer for 0-30-mol % and HFP.

[0080] Furthermore, a fluorine-containing segmentation polymer which is indicated by JP.81-49327.B is also contained as an example of a fluorine polymer.

[0081] It intervenes between the residue except this iodine atom, and this iodine atom and this residue, and if few, it will become this fluorine-containing segmentation polymer from the iodine atom isolated from the iodine compound which has fundamentally the iodine atom combined with the carbon atom, and this iodine compound considering two sorts of polymer chain segments (however, at least one of sorts [them] is a fluorine-containing polymer chain segment) as an indispensable constituent. If it puts in another way, the fluorine-containing segmentation polymer of this invention will become fundamentally considering the residue excluding this iodine atom from the iodine atom isolated from the iodine compound which has the iodine atom combined with the chain which consists of at least two sorts of polymer chain segments (however, at least one of sorts [them] is a fluorine-containing polymer chain segment), and the carbon atom which exists in the both ends, and this iodine compound as a part for an indispensable configuration, namely, the typical structure of a fluorine-containing segmentation polymer —

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chloride, allyl compound methyl ether, allyl compound isopropyl ether, the allyl compound octyl ether, etc. are raised as an example.

[0053] Moreover, in addition to this, styrene and a styrene derivative, and maleic-acid dialkyl ester are raised.

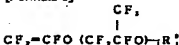
[0054] The non-fluorine monomer of fluorine-containing *** which has functional groups given in WO 95/No. 33782 pamphlet, such as a hydroxyl group, a carboxyl group, a carboxylate radical, an epoxy group, and a thiol group, is also copolymerizable further again.

[0055] The desirable structure of the fluorine polymer obtained by this invention can be divided roughly into two, what uses tetrafluoroethylene (TFE), hexafluoropropylene (HFP), or chlorotrifluoroethylene (CTFE) as a principal component as a fluorine-containing olefin, and the thing which uses vinylidene fluoride (VdF) as a principal component.

[0056] That is, the 1st group is a fluorine polymer which uses TFE, HFP, or CTFE as an indispensable component, copolymerizes a copolymerizable monomer besides the above if needed further, and is obtained.

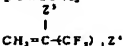
[0057] Setting to the aforementioned polymer, especially a desirable thing is VdF, hexafluoropropylene (HFP), hexafluoro isobutene, and formula: [0058] as other copolymerizable monomers.

[Formula 9]



[0059] For perfluoroalkyl radical of carbon numbers 1-8, (type Naka and R9 are the perfluoro vinyl ether shown by integer) of 0, or 1-5, and formula: [0060].

[Formula 10]



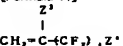
[0061] H or F:Z4 has [(type Naka and Z3) the fluorine-containing olefin and ethylene in which H or F is shown by integer) of 1-10, a propylene, 1-butene, desirable isobutene, etc.

[0062] As a still more detailed example of the fluorine polymer which uses TFE, HFP, or CTFE as a principal component. The homopolymer (PTFE) of TFE, the homopolymer of CTFE (PCTFE). The copolymer (FEP) of TFE and HFP, the copolymer of TFE and perfluoro vinyl ether (less than [10 mol %]) (PFA), It responds to TFE or CTFE, ethylene, and a pan at the need. A copolymer with a copolymerizable fluorine-containing olefin (E (C) TFE), HFP, ethylene, the copolymer of the shape of an elastomer which copolymerized TFE depending on the case, The copolymer of the shape of an elastomer which copolymerized TFE, the copolymer of the shape of an elastomer which copolymerized the propylene and TFE, and perfluoro vinyl ether (more than 15 mol %) etc. is raised preferably.

[0063] 0.3-5.0 mol % of the copolymer of perfluoro vinyl ether indicated in detail to be 95-99.7 mol % of TFE(s) as a PFA system copolymer in the inside of it by formula: $CF_2=CFOR^{10}$ (the inside of a formula and R10 are the perfluoroalkyl radical of carbon numbers 1-6) is desirable.

[0064] Moreover, as an (EC) TFE system copolymer, the fluorine-containing olefin 0 of the 3rd component used TFE or CTFE30 70-mol % and ethylene 30 - if needed [70 mol % / % and if needed] - 15-mol % of a copolymer are desirable. As a fluorine-containing olefin as the 3rd component, it is [0065].

[Formula 11]



[0066] (type Naka and Z3 can use the fluorine-containing olefin shown by integer) of 1-10, perfluoro vinyl ether, HFP, a hexafluoro isobutylene, etc., and H or F:Z4 is [H or F] [0067] especially.

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degree type-Q- [(A-B-)] — among [type F' The residue except an iodine atom, A and B. O from an iodine compound, respectively A polymer chain segment (it corrects and at least one of them is a fluorine-containing polymer chain segment), the iodine atom with which I was isolated from said iodine compound, and f' " can be expressed with] showing the number of the joint hands of Q.

[0082] Especially or more 5000 extent is [2000 or more] usually desirable [for a shaping application / generally / from the point of the own mechanical strength of a fluorine polymer / that it is not much low], for example, although suitable range especially differs and the molecular weight of the fluorine polymer obtained by this invention is not limited by the class of polymer, an application, and operation as number average molecular weight preferably. Moreover, especially or less 750000 extent is [1 million or less] usually preferably desirable [that it is not much high] from the point of a moldability.

[0083] The copolymer of the shape of resin which uses above TFE as a principal component in the example of a fluorine polymer further again. For example, when it is the fluorine polymer in which melting processing like PFA, FEP, and ETFE is possible, The melt flow value is the measurement temperature (for example, it PFA(s)) defined depending on the class of fluorine polymer. In FEP, it sets at 372 degrees C, and sets against 300 degrees C and a load (for example, 7kg) in ETFE, 0.01x10⁻² - 50x10⁻² ml/sec. It is 0.1x10⁻² - 10x10⁻² ml/sec. preferably [it is desirable and] to 0.05x10⁻² - 25x10⁻² ml/sec. and profit.

[0084] moreover, the case of a fluorine polymer meltable to solvents, such as DMF, such as a polymer of the shape of the shape of resin which consists of one or more sorts of the polymer of the shape of an elastomer which uses TFE or HFP as a principal component, the homopolymer of VdF and VdF, TFE and HFP, or CTFE, and an elastomer, and THF, for example, the determination-of-molecular-weight value of the polystyrene conversion by GPC, — it is — number average molecular weight — 2000-1 million — desirable — 5000-750000 — it is the thing of 10000-500000 especially preferably.

[0085] Moreover, in the case of the homopolymer (PTFE) of TFE, with a molecular weight of about 2000 to 1 million currently called the common-name low molecular weight PTFE from the oligomer-like thing thing and the high molecular weight object which cannot carry out melting processing further are included. The molecular weight in the case of the amount, PTFE of macromolecules can be manufactured to what is 1 million-10 million, and a maximum of 20 million about about, although it cannot specify.

[0086] The fluorine polymer latex of this invention is manufactured by the emulsion-polymerization method. Hereafter, first, polymerization conditions, an additive, etc. about a fluorine polymer at large are explained, and the suitable surfactant for each, polymerization conditions, an additive, etc. are explained for every fluorine polymer typical subsequently.

[0087] As an initiator used by the emulsion polymerization, although the usual radical initiator can be used A water-soluble initiator is adopted preferably. Specifically Peroxydisulfuric acid, hydrogen peroxides, such as an ammonium persulfate salt, organic peroxide (diisopropyl peroxy dicarbonate and di-n-propyl peroxy dicarbonate —), or these and sodium hydrogensulfates, such as t-butylperoxy persulfate. The redox initiator which consists of combination with reducing agents, such as a sodium thiosulfate and a hydroxy methane sulfonic acid; Still a small amount of iron to these, Dibasic-acid peroxides, such as inorganic system initiator [of the system which made ferrous salt, silver sulfate, etc. live together], or disuccinic acid peroxide, and JIGURU tar-acid peroxide; azobis isobutyramidine dithydrochloride etc. is raised. Moreover, the azo compound of water-soluble or oil solubility can be used similarly.

[0088] The description of this invention is that it uses the fluorine-containing surfactant of said formula (0 - IV) as a surfactant at the time of an emulsion polymerization (emulsifier). The amount used is about 0.01 - 10 % of the weight preferably 0.001 to 20 % of the weight in a sum total addition to a polymerization solvent (aqueous medium).

[0089] Furthermore, a well-known chain transfer agent, a buffer for pH, pH regulator, etc. can also be used if needed.

[0090] As a chain transfer agent, an isopentane, a diethyl malonate, ethyl acetate, n-hexane, a cyclohexane, a methanol, ethanol, a tert-butanol, a carbon tetrachloride, chloroform, a methylene

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chloride, a methyl chloride, fluorocarbon iodides (for example, CF₂I₂, CF₃I, H-(CF₂)₄-I, 2(CF₃)₂CFI, etc.), etc. can be used, for example.

[0091] The emulsion-polymerization conditions of this invention are suitably chosen by the class of fluorine polymer made into the purpose, a presentation, a polymerization initiator, etc., reaction temperature is 5-100 degrees C, and -20 degrees C - 150 degrees C of 10 or less MPaGs of polymerization pressure force are usually 7 or less MPaGs preferably.

[0092] Moreover, in manufacture of the fluorine polymer latex of this invention, there is especially no limit in the approach to the polymerization tank about each component (especially each component of a monomer, an initiator, and a chain transfer agent) to teach, and it may be carried out to it by the approach of teaching the whole quantity of the various components used from the beginning of a polymerization, or the approach of teaching a part or all of a component continuously or in division at a successive polymerization tub.

[0093] About 0.01-1 micrometer of fluorine polymer latexes obtained by the manufacture approach of this invention is the latex (aqueous emulsion) which contains preferably a 0.05-0.7-micrometer fluorine polymer particle by 20 - 40% of the weight of concentration about ten to 40% of the weight preferably, and number average particle diameter is stabilized by the distributed emulsification condition of a particle.

[0094] Coagulation or condensation can be presented, and it can collect, it can dry, and the fluorine-containing latex obtained in this way can be used as powder. Coagulation or condensation can adopt a well-known approach as it is conventionally. For example, the method (spray coagulation method) of evaporating water etc. is preferably adopted at the same time it makes a latex blow off from the approach of making a latex adding and carrying out coagulation (condensation) of the coagulating agent (floculant) to the bottom of stirring, the approach (freezing coagulation method) of carrying out coagulation by freezing and thawing a latex, the approach (machine coagulation method) of carrying out coagulation only by carrying out high-speed stirring of the latex mechanically, and a thin nozzle. Coagulant aid may be added as long as it requires. Desiccation may be left at a room temperature and may be dried in the state of heating to 250 degrees C.

[0095] The fluorine-containing latex obtained by this invention can also be prepared to the fluorine polymer aqueous dispersion liquid which condense or are further obtained by carrying out distributed stabilizing treatment, and the so-called dispersion.

[0096] An approach well-known as the concentration approach is adopted, and it is condensed by 40 - 80 % of the weight of concentration according to applications (for example, a water nature powder type coating, the binder for electrodes, water repellent for electrodes, etc.). Although the stability of dispersion may be spoiled by concentration, a distributed stabilizer may be added further in that case. As such a distributed stabilizer, said surfactant used by this invention and various kinds of other surfactants may be added. Although polyoxyethylene ether, such as nonionic surfactants, such as polyoxy alkyl ether, especially polyoxyethylene alkyl phenyl ether (for example, Triton X-100 (trade name) by ICI and Hoescht), the polyoxyethylene iso tridecyl ether (Despa Norian TOC by Nippon Oil & Fats Co., Ltd. (trade name)), and the polyoxyethylene propyl tridecyl ether, is raised as a desirable distributed stabilizer, they are not these things limited to seeing.

[0097] Moreover, distributed stabilizing treatment can be carried out without condensing depending on an application, and it can also prepare to fluorine polymer aqueous dispersion liquid with long pot life. What has the distributed stabilizer the same as the above to be used is raised.

[0098] The fluorine-containing latex obtained by this invention can carry out the seed polymerization of the ethylenic unsaturated monomer by using a VdF system copolymer as a seed further. As this ethylenic unsaturated monomer, the monomer and vinyl compound which have a functional group, for example are raised.

[0099] As a monomer with said functional group, for example an acrylic acid, a methacrylic acid, Methacrylic ester [such as an unsaturated-carboxylic-acid methyl acrylate /, such as an acrylic ester, methyl methacrylate], such as a maleic acid and a crotonic acid; Acrylamide, Methacrylamide, N-methylacrylamide, N-methylol acrylamide, N-butoxy methylacrylamide, N-methylol methacrylamide, Amide compounds, such as N-methyl methacrylamide and N-butoxy

methyl methacrylamide; Acrylic-acid hydroxyethyl, Hydroxyl-group content monomers, such as methacrylic-acid hydroxyethyl, acrylic-acid hydroxypropyl, and methacrylic-acid hydroxypropyl; Metathacryl acrylate, Epoxy group content monomers, such as glycidyl methacrylate, gamma-trimethoxysilane methacrylate, Silanol group content monomers, such as gamma-tris(hydroxysilane) methacrylate; although aldehyde group content monomers, such as an acrolein, etc. are raised and styrene, acrylonitrile, etc. are raised as said vinyl compound, for example. A point to the acrylic ester and/or methacrylic ester of compatibility with a VdF system copolymer are desirable. It is indicated by JP 7-50153A as the example.

[0100] An ethylenic unsaturated monomer carries out the 20-100 mass section polymerization of said VdF system seed polymer to the bottom of existence of the VdF system copolymer 100 mass section as said seed part.

[0101] That the aqueous dispersion liquid of the VdF system seed polymer of this invention blend additives, such as a pigment, a thickener, a dispersant, a defoaming agent, an antifreezing agent, and a membrane formation assistant, or the high molecular compound of further others — compounding — coating — service water — it can use as a sex coating.

[0102] Although explained according to a fluorine polymer typical next, explanation may be omitted when it is the same as that of the conditions and additive which were indicated in the above-mentioned general explanation.

[0103] (A) PTFE (G) — as a suitable surfactant — as a suitable surfactant CF₃OCF CF₂OCF (CF₃) COONH₄, CF₃OCF (CF₃) CF₂OCF (CF₃) COONH₄, CF₃CF₂OCF (CF₃) CF₂OCF (CF₃) COONH₄, CF₃CF₂OCF (CF₃) CF₂OCF (CF₃) COONH₄, H(CF₂CF₂)₂CH₂OCF(CF₃) COONH₄, HANOCO(CF₂CF₂)₂COONH₄, H(CF₂CF₂)₂CH₂OCOC(SO₃NH₄) CH₂COOCH₂(CF₂CF₂)₂H, (CF₃) H(CF₂CF₂)₂CH₂OCOC(SO₃Na) CH₂COOCH₂(CF₂CF₂)₂H etc. are raised.

[0104] Moreover, it is indicated that those who use the amount used below with critical micelle concentration (CMC) are suitable as indicated by JP 57-135A, JP 56-54016B, and JP 11-248807A. A reason is because the large needlelike particle of an aspect ratio is obtained above CMC (JP 48-34838B, JP 63-81104A).

[0105] Moreover, in order to secure the stability of the particle under polymerization, it is indicated that it is also effective in extent to which an aspect ratio does not become large to add the above-mentioned surfactant the middle.

[0106] (G) As a suitable polymerization condition polymerization initiator, it is independent or water-soluble organic peroxide, such as water-soluble persulfate (for example, ammonium persulfate), and disuccinic acid peroxide, jig RUTARU acid peroxide, is used in the form of such mixture. The addition approach can also carry out [teaching a package in early stages or] additional preparation to the middle, in order to obtain PTFE of the target physical properties.

[0107] Although a polymerization is usually performed in 10-90 degrees C about polymerization temperature, generally it is carried out at 65-90 degrees C from the decomposition temperature property of persulfate. Moreover, the example of a polymerization in temperature with a room temperature of 25 degrees C or less is also known by making it a redox system as indicated by JP 59-109534A. Moreover, controlling the crystallization degree of a polymerization object more changing polymerization temperature on the way is also known as indicated by JP 52-112688A.

[0108] Although the polymerization in 0.1 - 0.2MPaG is also possible if the polymerization pressure force disregards productivity, a polymerization is usually performed in the range of 0.3-0.4MPa.

[0109] (ii) As an additive in the middle of a suitable additive polymerization, it is indicated by JP 57-135A by stages by adding aromatic amine, about 0.7-20 ppm of aromatic series hydroxy compounds etc., etc. to the water which is a polymerization medium in the middle of the polymerization that it has a particulate structure with the specific gravity of the last particle smaller than the specific gravity of a particle core part, and the PTFE particle of the colloid whose path is 100-500nm can be obtained. Thereby, polymer powder with high molecular weight with the small specific gravity of the last object is obtained. Since these are excellent in paste extrusion nature, mechanical strength, etc., a product with good mold-goods physical properties, such as extension porosity film, a tube, a rod, and a film, is obtained.

[0110] (B) Although it is Denaturation PTFE, next manufacture of denaturation PTFE fine powder, it is manufactured by the emulsion-polymerization method like non-denaturated PTFE fine powder.

[0111] (i) to a modifier and the amount denaturation monomer of denaturation, like a publication at JP 4-3785B CF₂=CF-CF₃ (HFP), ClCF=CF₂ (CTFE), General formula: X(CF₂)_nOCF=CF₂ (among a formula), such as C₄F₉ CH=CH₂ X is Cl and H, F, or n is integer [of 1-8], or C₃F₇ (OCF₂CF₂CF₂) m(OCF(CF₃) CF₂) tOCF=CF₂ (among a formula). The fluoro alkyl vinyl ether compound in which m is shown by the integer of 0-2, and t is shown for the integer of 0-2, for example, perfluoro propyl vinyl ether, (PPVE), and perfluoromethylvinylether (PMVE) are raised. In addition, ethylene, a propylene, the methyl vinyl ether, vinyl acetate, etc. are raised with vinylidene fluoride and vinyl fluoride and a hydrocarbon system.

[0112] As for these denaturation monomer, independent or being used in the form of mixture are common.

[0113] Moreover, the addition stage of a denaturation monomer can also choose an addition stage freely according to the purposes, such as an addition and continuation addition, in the middle of initial package addition. This becomes possible to control [for the purpose of the denaturation part of a polymer particle], for example, the surface section or a core is denaturated — or the surface section from a particle core — or it is possible to denaturate from the surface section in inclination to a core etc.

[0114] Moreover, the denaturation monomer content in the PTFE polymer after a polymerization becomes controllable by changing the denaturation monomer charge into a polymerization tank according to an application. Usually, it is known that the range of the denaturation monomer content in an after [a polymerization] polymer is about 0.001-20 mol %.

[0115] (ii) — as a suitable surfactant — as a suitable surfactant CF₃OCF CF₂OCF (CF₃) COONH₄, CF₃OCF (CF₃) CF₂OCF (CF₃) COONH₄, CF₃CF₂OCF (CF₃) CF₂OCF (CF₃) COONH₄, CF₃CF₂OCF (CF₃) CF₂OCF (CF₃) COONH₄, H(CF₂CF₂)₂CH₂OCF(CF₃) COONH₄, HANOCO(CF₂CF₂)₂COONH₄, H(CF₂CF₂)₂CH₂OCOC(SO₃NH₄) CH₂COOCH₂(CF₂CF₂)₂H, (CF₃) H(CF₂CF₂)₂CH₂OCOC(SO₃Na) CH₂COOCH₂(CF₂CF₂)₂H etc. are raised.

[0116] the amount used — an aqueous medium — receiving — 0.01 to 1 mass % — it is 0.02 to 0.5 mass % preferably.

[0117] (iii) As a suitable polymerization condition polymerization initiator, it is independent or water-soluble organic peroxide, such as water-soluble persulfate (for example, ammonium persulfate), and disuccinic acid peroxide, jig RUTARU acid peroxide, is used in the form of such mixture. The addition approach can also carry out [teaching a package in early stages or] additional preparation to the middle, in order to obtain PTFE of the target physical properties.

[0118] Although a polymerization is usually performed in 10-90 degrees C about polymerization temperature, generally it is carried out at 65-90 degrees C from the decomposition temperature property of persulfate. Moreover, the example of a polymerization in temperature with a room temperature of 25 degrees C or less is also known by making it a redox system like JP 59-109534A. Moreover, controlling the crystallization degree of a polymerization object more changing polymerization temperature on the way is also known like JP 52-112688A.

[0119] Although the polymerization in 0.1 - 0.2MPaG is also possible if the polymerization pressure force disregards productivity, a polymerization is usually performed in the range of 0.3-0.4MPa.

[0120] (iv) As an additive in the middle of a suitable additive polymerization, it is indicated by JP 57-135A by stages by adding aromatic amine, about 0.7-20 ppm of aromatic series hydroxy compounds etc., etc. to the water which is a polymerization medium in the middle of the polymerization that it has a particulate structure with the specific gravity of the last particle smaller than the specific gravity of a particle core part, and the PTFE particle of the colloid whose path is 100-500nm can be obtained. Thereby, polymer powder with high molecular weight with the small specific gravity of the last object is obtained. Since these are excellent in paste extrusion nature, mechanical strength, etc., a product with good mold-goods physical properties, such as extension porosity film, a tube, a rod, and a film, is obtained.

[0121] (C) As an FEP(i) monomer presentation presentation, the thing of TFE 60 - 95 mass %, and HFP 5 - 40 mass % is used. The thing of 85 to TFE90 mass %, and HFP 10 - 15 mass % is used preferably. Moreover, what perfluoro vinyl ether was 0.5-2 mass % Used [what], and denaturated it to the whole as the 3rd component to these can also be used.

[0122] (ii) — as a suitable surfactant — as a suitable surfactant CF₃OCF CF₂OCF (CF₃) COONH₄, CF₃OCF (CF₃) CF₂OCF (CF₃) COONH₄, CF₃CF₂OCF (CF₃) CF₂OCF (CF₃) COONH₄, CF₃CF₂OCF (CF₃) CF₂OCF (CF₃) COONH₄, H(CF₂CF₂)₂CH₂OCF(CF₃) COONH₄, HANOCO(CF₂CF₂)₂COONH₄, H(CF₂CF₂)₂CH₂OCOC(SO₃NH₄) CH₂COOCH₂(CF₂CF₂)₂H, (CF₃) H(CF₂CF₂)₂CH₂OCOC(SO₃Na) CH₂COOCH₂(CF₂CF₂)₂H etc. are raised.

[0123] (iii) The polymerization pressure force has [suitable polymerization condition polymerization temperature / 60-100 degrees C] desirable 0.7 - 4.5MPaG.

[0124] (iv) As a suitable additive chain transfer agent, a cyclohexane, a methanol, ethanol, a carbon tetrachloride, chloroform, a methylene chloride, a methyl chloride, etc. are desirable, and an ammonium carbonate, disodium phosphate, etc. are desirable as a buffer for pH.

[0125] (D) As a PFA(ii) monomer presentation presentation, TFE 95.997-mol % and perfluoro vinyl ether 0.3 - 5.0-mol % of a thing are used. 0.5-2.0 mol % of the thing of 98-99.5 mol % and perfluoro vinyl ether of TFE(a) is used preferably. If it considers as perfluoro vinyl ether, the perfluoroalkyl vinyl ether shown by formula: CF₂=CFOR' (the inside R' of a formula is the perfluoroalkyl radical of carbon numbers 1-8) is desirable.

[0126] (ii) — as a suitable surfactant — as a suitable surfactant CF₃OCF CF₂OCF (CF₃) COONH₄, CF₃OCF (CF₃) CF₂OCF (CF₃) COONH₄, CF₃CF₂OCF (CF₃) CF₂OCF (CF₃) COONH₄, CF₃CF₂OCF (CF₃) CF₂OCF (CF₃) COONH₄, H(CF₂CF₂)₂CH₂OCF(CF₃) COONH₄, HANOCO(CF₂CF₂)₂COONH₄, H(CF₂CF₂)₂CH₂OCOC(SO₃NH₄) CH₂COOCH₂(CF₂CF₂)₂H, (CF₃) H(CF₂CF₂)₂CH₂OCOC(SO₃Na) CH₂COOCH₂(CF₂CF₂)₂H etc. are raised.

[0127] (iii) The polymerization pressure force has [suitable polymerization condition polymerization temperature / 60-100 degrees C] desirable 0.7 - 2.5MPaG.

[0128] (iv) As a suitable additive chain transfer agent, a cyclohexane, a methanol, ethanol, a carbon tetrachloride, chloroform, a methylene chloride, a methyl chloride, methane, ethane, etc. are desirable, and an ammonium carbonate, disodium phosphate, etc. are desirable as a buffer for pH.

[0129] (E) As an ETFE(i) monomer presentation preparation presentation — TFE / ethylene mol ratio 50 / 50 - 99/1 — carrying out — this — receiving — a denaturation monomer — 0 - 20 mol % — use, desirable — TFE / ethylene mol ratio 70 / 30 - 98/2 — carrying out — this — receiving — a denaturation monomer — 4-10-mol % — it uses. As a denaturation monomer, they are 2, 3, 4, 4, 5, and 5-heptafluoro-1-pentene (CH₂CF₂CF₂CF₂CF₂H) or 2-trifluoromethyl - It is desirable to use 1, 3, and 3-trifluoro propene (CF₃)₂C=CH₂.

[0130] (ii) — as a suitable surfactant — as a suitable surfactant CF₃OCF CF₂OCF (CF₃) COONH₄, CF₃OCF (CF₃) CF₂OCF (CF₃) COONH₄, CF₃CF₂OCF (CF₃) CF₂OCF (CF₃) COONH₄, CF₃CF₂OCF (CF₃) CF₂OCF (CF₃) COONH₄, H(CF₂CF₂)₂CH₂OCF(CF₃) COONH₄, HANOCO(CF₂CF₂)₂COONH₄, H(CF₂CF₂)₂CH₂OCOC(SO₃NH₄) CH₂COOCH₂(CF₂CF₂)₂H, (CF₃) H(CF₂CF₂)₂CH₂OCOC(SO₃Na) CH₂COOCH₂(CF₂CF₂)₂H etc. are raised.

[0131] (iii) The polymerization pressure force has [suitable polymerization condition polymerization temperature / 20-100 degrees C] desirable 0.5 - 0.8MPaG. (BR) [0132] (iv) As a suitable additive chain transfer agent, a cyclohexane, a methanol, ethanol, a carbon tetrachloride, chloroform, a methylene chloride, a methyl chloride, etc. are used preferably.

[0133] (F) PVdF (i) — as a suitable surfactant — as a suitable surfactant CF₃OCF CF₂OCF (CF₃) COONH₄, CF₃OCF (CF₃) CF₂OCF (CF₃) COONH₄, CF₃CF₂OCF (CF₃) CF₂OCF (CF₃) COONH₄, CF₃CF₂OCF (CF₃) CF₂OCF (CF₃) COONH₄, H(CF₂CF₂)₂CH₂OCF(CF₃) COONH₄, HANOCO(CF₂CF₂)₂COONH₄, H(CF₂CF₂)₂CH₂OCOC(SO₃NH₄) CH₂COOCH₂(CF₂CF₂)₂H, (CF₃) H(CF₂CF₂)₂CH₂OCOC(SO₃Na) CH₂COOCH₂(CF₂CF₂)₂H etc. are raised.

[0176] Perfluoro adipic acid 2 ammonium 162g (0.50 mole) was obtained by adding 63g (1.04 mole) of aqueous ammonia, and 100g of water to 150g (0.517 mole) of synthetic example 3 perfluoro adipic acid 28%, and removing water by distillation, 97% of yield.

[0177] When the surface tension of the water solution of this ammonium salt was measured, by 10 mass % concentration, 66.5 mN/m, therefore critical micelle concentration was not measured by 69.6 mN/m and 0.1 mass % concentration with 47.8 mN/m and 1 mass % concentration, and were not measured by 87.6 mN/m and 0.001 mass % concentration with 70.8 mN/m and 0.01 mass % concentration. The melting point T_G/DTA measurement of this ammonium salt was [260 degrees C and 50% decomposition temperature of 147 degrees C and 10% decomposition temperature] 280 degrees C.

[0178] The boiling reflux of the synthetic examples 42, 2, 3, 3, 4, 4, and 5, 5-octadecyl-1-pentanol 116g (0.50 mole) and 23.5g (0.24 mole) of maleic anhydrides, and the 9.5g (0.05 mole) of the p-toluenesulfonic acid monohydrates is carried out in 1L of toluene, and the separating water was removed with azeotropy. After baking was stopped for 21 hours and it washed in cold water at 70 degrees C. By carrying out reduced pressure Shimo fractional distillation of the toluene layer, 103g (2, 2, 3, 3, 4, 4, 5, and 5-octadecyl-1-pentyl) (0.19 mole) of maleic-acid screws was obtained. 1 H-NMR(THF-d8): 6.13 (t, 2H, HC=CH2) delta 4.74 (t, 4H, CH2O), 6.41 (s, 2H, CH=), [0179] The solution which melted maleic-acid bis(2, 2, 3, 3, 4, 4, 5, and 5-octadecyl-1-pentyl) 50.0g (0.092 mole) to 500ml 1,4-dioxane, and melted 10.0g (0.096 mole) of sodium hydrogensulfates in 200ml water was added, and boiling reflux was carried out for three days. Generated precipitate was carried out the exception with the glass filter, and it washed by 50-degree C 1,4-dioxane, it washed and dried by a small amount of water and tetrahydrofuran after that, and 52.5g (0.081 mole) of succinic-acid bis(2, 2, 3, 3, 4, 4, 5, and 5-octadecyl-1-pentyl)-2-sulfonic-acid sodium was obtained. 1 H-NMR(acetone-d6): delta 3.30 (d, 2H, and CH2CO), 4.53 (t, 2H, CHCO), 4.80 (t, 4H, CH2O), 7.72 (t, 2H, HC=CH2).

[0180] Example 1 (polymerization example of a PTFE fine powder latex)

3.0g of surfactants of 120g (melting point of 56 degrees C) and formula:CF3CF2CF2OCF(CF3)CF2OCF(CF3) COONH4 was taught to the autoclave with a support stirring aerofoil made from the stainless steel of 6L inner capacity for 3L of deionized water, and paraffin wax, and as an initiator, ammonium persulfate (APS) was put into it so that it might become the concentration of 10 ppm to water. Having pressed fit until it became 0.88 MPa by the TFE monomer after the 2 times permutated by the TFE monomer, and maintaining stirring at 250rpm, after carrying out the nitrogen purge of the inside of an autoclave enough, it heated to 70 degrees C and the polymerization was started. Since the pressure in a polymerization system declined with advance of a polymerization, additional press fit of the TFE was carried out, and the polymerization pressure force was maintained at 0.78MPa(s). After polymerization initiation, when polymer polymerization was 10.5 mass %, 2 ppm of hydroquinone were added to water, and the polymerization was continued as it was. When polymer was reached 24.5 mass %, TFE was omitted, the polymerization was suspended and the PTFE latex of this invention was obtained. [0181] The number average particle diameter of the PTFE particle in this latex (primary particle) was 300nm.

[0182] After diluting the obtained PTFE latex with water to the solid content concentration 12 - 13 mass %, it stirred mechanically and condensed, and after recovery, it dried at 130 degrees C for 18 hours, and the PTFE fine powder of this invention was obtained (standard specific gravity: 2.17).

[0183] It mixed with the shaping assistant (IP1620 (trade name) obtained from Idemitsu Petrochemistry), this PTFE fine powder was pasted, and paste extrusion shaping was presented. Paste extrusion was performed the following condition.

Extruder: The autograph by Shimadzu Corp.

Reduction ratio (R/R): 100 [0184] It was 37MPa, when heating baking of the obtained extrusion-molding object was carried out for 5 minutes at 380 degrees C, it considered as mold goods and the tensile strength of this thing was investigated.

[0185] In addition, the measuring method of each physical properties is as follows.

Standard specific gravity: ASTM According to D 1457-69, it measures by the sinking method. A

test portion fills up metal mold (25mmphi) with 12g of fluorine polymer powder, and produces it by imposing the load of 20MPa and holding for 2 minutes.

The diameter of a primary particle of a fluorine polymer latex : The permeability of 550nm incident light [as opposed to / dilute the fluorine polymer (PTFE) particle latex after an emulsion polymerization with water to solid content concentration 0.15 mass % and / the unit length of these diluted aqueous dispersion liquid]. The diameter of a primary particle is determined using the calibration curve which plotted and created the several set semi-diameter mean particle diameter which measured and determined unidirectional particle diameter from the transmission electron microscope photograph from the value of the above-mentioned permeability (550nm) measured about each sample.

Tensile strength of mold goods: JIS K It measures according to 5400.

[0186] A result is indicated to Table 1.

[0187] the surfactant of example 2 example 1 — formula: — it changed into H(CF2CF2)2CH2OCF(CF3) COONH4, the charge and the polymerization formula were performed similarly, and the PTFE latex was obtained.

[0188] the surfactant of example 3 example 1 — formula: — it changed into H4NOCOC(CF2CF2)2COONH4, the charge and the polymerization formula were performed similarly, and the PTFE latex was obtained.

[0189] the surfactant of example 4 example 1 — formula: — it changed into H(CF2CF2)2CH2OCOC(CH3O3Na) CH2COOCH2(CF2CF2)2H, the charge and the polymerization formula were performed similarly, and the PTFE latex was obtained.

[0190]

[Table 1]

表1: PTFEファイナパウダーラテックスの重合実験例

実験例	界面活性剤	温度 [°C]	一次粒子径 [nm]	ポリマー 比重	成形体の 引張り強度 [MPa]
実験例1	C ₁₂ F ₂₁ FCF ₂ OCF(CF ₃)CF ₂ OCF(CF ₃)COONH ₄	70	300	2.17	37
実験例2	H(CF ₂ CF ₂) ₂ CH ₂ OCF(CF ₃)COONH ₄	70	355	2.16	36
実験例3	H ₄ NOCOC(CF ₂ CF ₂) ₂ COONH ₄	70	315	2.155	35.5
実験例4	H(CF ₂ CF ₂) ₂ CH ₂ OCOC(CH ₃ O ₃ Na)CH ₂ COOCH ₂ (CF ₂ CF ₂) ₂ H	70	308	2.178	35.8

[0191] Example 5 (polymerization of a denaturation PTFE fine powder latex)

They are 3L of deionized water, and paraffin wax to the autoclave with a support stirring aerofoil from the stainless steel of 6L inner capacity. Having prepared 3.0g of surface active agents of 100g (melting point of 56 degrees C), and formula:CF3CF2CF2OCF(CF3) CF2OCF(CF3) COONH4, and maintaining stirring at 280rpm, after nitrogen permuted the TFE monomer permutated twice 3 times, the pressure up of the inside of an autoclave was carried out to 0.68MPa(s) by the TFE monomer.

[0192] Next, the water solution which melted 0.3g (APS) of 11.25mg ammonium persulfates in 20 cc water continuously in perfluoro propyl vinyl ether (PPVE), and the water solution which melted 360mg disuccinic acid peroxide (DSP) are pressed fit by the TFE monomer, and autoclave internal pressure is set to 0.78MPa(s). Although a reaction advances accelerative, reaction temperature keeps 70 degrees C and rotating speed constant 280 rpm. A TFE monomer is continuously accelerated so that internal pressure may be maintained at 0.78MPa(s).

[0193] After adding an initiator, when the TFE monomer consumed at the reaction amounts to 1300g, supply and stirring of a TFE monomer are stopped. The gas in an autoclave is emitted until internal pressure is immediately set to 0.18MPa(s), it changes to Rhine of the mixed monomer of CTFE containing 1.5-mol % of CTFE subsequently prepared beforehand, and TFE, and continuation supply is carried out. That is, a mixed monomer is maintained to internal pressure 0.78MPa, stirring is maintained to 280rpm, and it reacts succeeding.

[0194] When the consumption of a mixed monomer amounts to 130g, supply and stirring of a mixed monomer are stopped, a monomer is emitted until the inside of an autoclave becomes ordinary pressure immediately, contents are taken out, and a reaction is ended.

[0195] When the gas chromatography analyzed the mixed gas under reaction by the mixed monomer (namely, stage of reaction of the shell of a particle), and in an autoclave, it was about 0.9-1.1-mol %. If the consumption of the TFE consumption pair mixing monomer of the ***** product of the particle in this reaction is calculated, it will become 1300:130, 9:1 (i.e.,).

[0196] When evaporation to dryness of a part of last latex was carried out and polymer density measurement of the solid content was carried out, it was 32 mass %. The mean particle diameter of a latex was 230nm.

[0197] It was 2.178, when coagulation desiccation of the obtained latex was carried out like the example 1 and specific gravity was measured. In addition, when PPVE and the CTFE content in a polymer were measured, they were 0.02 mass % and 0.09 mass %. The value to which the CTFE content multiplied the ratio of the absorbance of 2360cm⁻¹ to the absorbance of 957cm⁻¹ of an infrared-absorption spectral band by 0.58, and the PPVE content determined the value which multiplied the ratio of the absorbance of 955cm⁻¹ and 2360cm⁻¹ by 0.95 as the content in a polymer.

[0198] In addition, the measuring method of each physical properties is the same as the approach of example 1 publication.

Standard specific gravity: ASTM According to D 1457-69, it measures by the sinking method. A test portion fills up metal mold (25mmphi) with 12g of fluorine polymer powder, and produces it by imposing the load of 20MPa and holding for 2 minutes.

The diameter of a primary particle of a fluorine polymer latex : The permeability of 550nm incident light [as opposed to / dilute the fluorine polymer (PTFE) particle latex after an emulsion polymerization with water to solid content concentration 0.15 mass %, and / the unit length of these diluted aqueous dispersion liquid]. The diameter of a primary particle is determined using the calibration curve which plotted and created the several set semi-diameter mean particle diameter which measured and determined unidirectional particle diameter from the transmission electron microscope photograph from the value of the above-mentioned permeability (550nm) measured about each sample.

Tensile strength of mold goods: JIS K It measures according to 5400.

[0199] the surfactant of example 6 example 5 — formula: — it changed into H(CF2CF2)2CH2OCF(CF3) COONH4, and the polymerization was performed like the example 5 except having changed APS into 12.3mg and having changed polymerization temperature into 85 degrees C for the charge of DSP at 180mg.

[0200] the surfactant of example 7 example 5 — formula: — the polymerization was performed like the example 5 except having changed into HANOCOC(CF2CF2)2COONH4.

[0201] the surfactant of example 8 example 5 — formula: — it changed into H(CF2CF2)2CH2OCOC(CH3O3Na) CH2COOCH2(CF2CF2)2H, and the polymerization was performed like the example 5 except having changed APS into 12.3mg and having changed polymerization temperature into 85 degrees C for the charge of DSP at 180mg.

[0202]

[Table 2]

表2: 変性PTFEファイナパウダーラテックスの重合実験例

界面活性剤	温度 [°C]	DSP [mg]	APS [mg]	一次粒子径 [nm]	ポリマー 比重	成形体の 引張り強度 [MPa]
実験例5 C ₁₂ F ₂₁ FCF ₂ OCF(CF ₃)CF ₂ OCF(CF ₃)COONH ₄	70	340	11.25	315	2.178	39
実験例6 H(CF ₂ CF ₂) ₂ CH ₂ OCF(CF ₃)COONH ₄	85	160	7.3	225	2.18	38
実験例7 H ₄ NOCOC(CF ₂ CF ₂) ₂ COONH ₄	70	340	11.25	300	2.18	36.5
実験例8 H(CF ₂ CF ₂) ₂ CH ₂ OCOC(CH ₃ O ₃ Na)CH ₂ COOCH ₂ (CF ₂ CF ₂) ₂ H	85	160	11.3	280	2.181	3.7

[0203] Example 9 (preparation of PTFE and denaturation PTFE concentration dispersion)

To the PTFE dispersion liquid (polymer concentration: 24 mass %) obtained in the example 1, it is a nonionic surfactant. Addition of the C13H27O(CH2CH2O) nH (n= 8.5, 49 degrees C of cloudy points) (Nippon Oil & Fats make; trade name DISU per Norian TOC) is carried out 10% (solid content mass for a polymer), and the aqueous ammonia of sufficient amount to raise pH of dispersion liquid from about 3 to about 10 further is added. The obtained dispersion liquid are quietly stirred for several minutes, and it heats at 55 degrees C, and puts for 24 hours. Those with 65 mass % and its Despa Norian TOC content of the solid content concentration of the concentration dispersion liquid which removed the produced transparent supernatant layer and were obtained were 3.4% on the basis of the mass of dispersion liquid. Despa Norian TOC was further added about 2.6% in 1L of samples of these dispersion liquid, and about 60% of solid content and a surfactant content were made into about 6%.

[0204] To the PTFE dispersion liquid (polymer concentration: 24 mass %) obtained in the example 10 example 2, it is a nonionic surfactant. Addition of the C13H27O(CH2CH2O) nH (n= 9.5, 58.8 degrees C of cloudy points) is carried out 10% (solid content mass for a polymer), and the aqueous ammonia of sufficient amount to raise pH of dispersion liquid from about 3 to about 10 further is added. The obtained dispersion liquid are quietly stirred for several minutes, and it heats at 70 degrees C, and puts for 24 hours. Those with 66 mass % and its Despa Norian TOC content of the solid content concentration of the concentration dispersion liquid which removed the produced transparent supernatant layer and were obtained were 3.5% on the basis of the mass of dispersion liquid. Despa Norian TOC was further added about 2.5% in 1L of samples of these dispersion liquid, and about 60% of solid content and a surfactant content were made into about 6%.

[0205] Using the PTFE dispersion liquid obtained in the 11 to example 18 examples 3-8, it condensed by the same formula as an example 10, and concentration liquid as shown in Table 3 was obtained.

[0206] Like examples 9 and 10, it prepared so that the solid content concentration of a polymer might become about 6% about a surfactant content about 60%.

[0207]

[Table 3]

表3: PTFE及び変性PTFE濃縮液の製造実験例

実験例	元のPTFE 分散液	界面活性剤	濃縮温度 [°C]	濃縮後の 一次粒子径 [nm]	濃縮後のノニオン性 界面活性剤濃度 [質量% 対ポリマー 固相分質量]
実験例9	実験例1で作成	C ₁₃ H ₂₇ O(CH ₂ CH ₂ O) _{8.5} H (n=8.5, 49°C)	55	65	2.4
実験例10	実験例2で作成	C ₁₃ H ₂₇ O(CH ₂ CH ₂ O) _{9.5} H (n=9.5, 58.8°C)	70	66	2.5
実験例11	実験例3で作成	同上	70	67	2.3
実験例12	実験例4で作成	同上	70	65	2.6
実験例13	実験例5で作成	同上	70	70	2.1
実験例14	実験例6で作成	同上	70	71	1.9
実験例15	実験例7で作成	同上	70	69	2.1
実験例16	実験例8で作成	同上	70	68	2.2

[0208] Example 17 (manufacture of a non-fibril plasticity PTFE polymer particle)

9.0g of surfactants of 3L [of deionized water] and paraffin was 120g (melting point of 56 degrees C) and formula:CF3CF2CF2OCF(CF3) CF2OCF(CF3) COONH4 was taught to the autoclave with a support stirring aerofoil made from the stainless steel of 6L inner capacity. It heated to 70 degrees C, having pressed fit until it set after the 2 times permutated by the TFE

monomer and was set to 1.0MPa(a) by the TFE monomer, and maintaining stirring at 250rpm, after carrying out the nitrogen purge of the inside of an autoclave enough. As a chain transfer agent, by ordinary pressure, 40 cc water solution which melted 300mg (APS) of ammonium persulfate which are 15g perfluoro propyl vinyl ether (PPVE) and a polymerization initiator considering 130 cc ethane as a comonomer was prepared in the system, and the reaction was started. During the reaction, since the pressure in a polymerization system declined with advance of a polymerization, additional press fit of the TFE was carried out, and the polymerization pressure was maintained at 1.0(=0.05) MPa. After polymerization initiation, when TFE monomer consumption amounted to 530g, TFE supply and stirring were stopped, and the internal pressure of a tub was emitted to ordinary pressure, and the reaction was ended. Polymer solid content concentration was 15%. The number average particle diameter of the PTFE particle in this latex (primary particle) was 85nm.

[0209] The ammonium carbonate was added, it dried at 130 degrees C for 16 hours, and the obtained PTFE latex was made powdered, after carrying out condensation recovery. When paste extrusion was performed, the extrusion object is discontinuous and did not have the reinforcement according to fibrillation for whether it being π , and elongation.

[0210] After using this latex, adding Triton X-100 (made in Iom & Haas) about 6% to PTFE solid content as a nonionic surface active agent and aqueous ammonia's adjusting pH to 9, usable concentration PTFE dispersion was producible to the water repellent for cells by condensing so that moisture may be evaporated under reduced pressure and polymer solid content may become 60%. Particle diameter was 85nm before concentration.

[0211] The surfactant of 18 to example 17 was changed into the surfactant given in Table 4, the charge and the polymerization formula were performed similarly, and the PTFE latex was obtained. In addition, it checked that it could condense to 60% of polymer solid content concentration about the examples 18-20 as well as an example 17. The experimental result of examples 17-20 was collectively indicated to Table 4.

[0212]

[Table 4]

表 4 : 非フッ素系樹脂 PTFE 重合体分散液の製造例

例	界面活性剤	温度(°C)	一次粒子径(nm)
実施例17	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ COONH ₄	70	85
実施例18	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ COONH ₄	70	180
実施例19	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ COONH ₄	70	120
実施例20	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ COONH ₄	70	91

[0213] Example 21 (emulsion polymerization of FEP)
CF₃CF₂CF₂CF₂CF₂CF₂COONH₄ was taught as 1500g of deionized water, and a surfactant, and 1000 ppm of ammonium carbonates were taught to the autoclave with an agitator made from the stainless steel of 3l inner capacity as 7500 ppm and a buffer for pH. After carrying out the nitrogen purge of the autoclave enough, it stirred by 600rpm and heated to 80 degrees C. Then, HFP gas and TFE gas were pressed fit and the gaseous layer section presentation was made into TFE/HFP=25/75-mole by tub internal pressure 0.8MPaG. As an initiator, when ammonium persulfate (APS) was prepared so that it might become the concentration of 500 ppm, the polymerization reaction started it, and the fall of a pressure was seen. During the polymerization reaction, additional press fit of the TFE/HFP=91/9-mole % of mixed gas was carried out, and tub internal pressure 0.8MPaG was maintained. Moreover, since a reaction rate fell by decomposition reduction of an initiator, 200 ppm of APSs were added every 3 hours after reaction initiation, and the rate of polymerization was made to fixed-size. 20 hours after polymerization initiation, stirring was stopped, the polymerization was suspended, the TFE/HFP gas in a tub was emitted, and it cooled to the room temperature.

[0214] The solid content concentration of the FEP latex of obtained this invention was 20.5

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seen. During the polymerization reaction, additional press fit of the TFE gas was carried out, and tub internal pressure 0.8MPaG was maintained. 5 hours after polymerization initiation, stirring was stopped, the polymerization was suspended, the TFE gas in a tub was emitted, and it cooled to the room temperature.

[0224] The solid content concentration of the PFA latex of obtained this invention was 11.0 mass %, and the number average particle diameter of a primary particle was 131nm. Moreover, when the white polymer obtained by coagulating this latex using a nitric acid was analyzed, it was PFA of PPVE5.5 mass % and the melt flow values in 372 degree C and Sg load were 0.019 ml/sec.

[0225] Example 26 (emulsion polymerization of PFA)

H(CF₂CF₂)₂CH₂COCH₂(CF₃) COONH₄ was used as a surfactant, and also the same actuation as an example 25 was performed, and the emulsion polymerization of PFA was performed.

[0226] The solid content concentration of the PFA latex of obtained this invention was 12.0 mass %, and the number average particle diameter of a primary particle was 129nm. Moreover, when the white polymer obtained by coagulating this latex using a nitric acid was analyzed, it was PFA of PPVE5.8 mass % and the melt flow values in 372 degree C and Sg load were 0.022 ml/sec.

[0227] Example 27 (emulsion polymerization of PFA)

HANOCO(CF₂CF₂)₂COONH₄ was used as a surfactant, and also the same actuation as an example 25 was performed, and the emulsion polymerization of PFA was performed.

[0228] The solid content concentration of the PFA latex of obtained this invention was 11.5 mass %, and the number average particle diameter of a primary particle was 135nm. Moreover, when the white polymer obtained by coagulating this latex using a nitric acid was analyzed, it was PFA of PPVE5.7 mass % and the melt flow values in 372 degree C and Sg load were 0.017 ml/sec.

[0229] Example 28 (emulsion polymerization of PFA)

H(CF₂CF₂)₂CH₂COCH₂(SO₃Na) CH₂COOCH₂(CF₂CF₂)₂H were used as a surfactant, and also the same actuation as an example 25 was performed, and the emulsion polymerization of PFA was performed.

[0230] The solid content concentration of the PFA latex of obtained this invention was 11.5 mass %, and the number average particle diameter of a primary particle was 125nm. Moreover, when the white polymer obtained by coagulating this latex using a nitric acid was analyzed, it was PFA of PPVE5.8 mass % and the melt flow values in 372 degree C and Sg load were 0.025 ml/sec.

[0231] The experimental result of examples 25-28 was collectively indicated to Table 6.

[0232]

[Table 6]

表 6

例	ラテックス	最新ポリマー		
		固形分濃度(質量%)	一次平均粒子径(nm)	PPVE含有率(質量%)
実施例25	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ COONH ₄	11.0	131	5.5
実施例26	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ COONH ₄	12.0	129	5.8
実施例27	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ COONH ₄	11.5	135	5.7
実施例28	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ COONH ₄	11.5	125	5.8

[0233] Example 29 (emulsion polymerization of PVdF)

After it taught 45ml of ion exchange water, and 0.25g of emulsifiers to the autoclave made from stainless steel of 100ml content volume and nitrogen permuted with it enough, VdF4.8g was taught by the vacuum. The autoclave was put into the 70-degree C constant temperature bath shaker, and it shook until the pressure was fixed (2.8MPaG). When the pressure became fixed,

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mass %, and the number average particle diameter of a primary particle was 180nm. Moreover, when the white polymer obtained by coagulating this latex using a nitric acid was analyzed, it was FEP of HFP12.3 mass % and the melt flow values in 372 degree C and Sg load were 0.0056 ml/sec.

[0215] Example 22 (emulsion polymerization of FEP)

H(CF₂CF₂)₂CH₂COCH₂(CF₃) COONH₄ was used as a surfactant, and also the same actuation as an example 21 was performed, and the emulsion polymerization of FEP was performed.

[0216] The solid content concentration of the FEP latex of obtained this invention was 19.5 mass %, and the number average particle diameter of a primary particle was 190nm. Moreover, when the white polymer obtained by coagulating this latex using a nitric acid was analyzed, it was FEP of HFP12.1 mass % and the melt flow values in 372 degree C and Sg load were 0.0082 ml/sec.

[0217] Example 23 (emulsion polymerization of FEP)

HANOCO(CF₂CF₂)₂COONH₄ was used as a surfactant, and also the same actuation as an example 21 was performed, and the emulsion polymerization of FEP was performed.

[0218] The solid content concentration of the FEP latex of obtained this invention was 18.8 mass %, and the number average particle diameter of a primary particle was 210nm. Moreover, when the white polymer obtained by coagulating this latex using a nitric acid was analyzed, it was FEP of HFP11.7 mass % and the melt flow values in 372 degree C and Sg load were 0.0047 ml/sec.

[0219] Example 24 (emulsion polymerization of FEP)

H(CF₂CF₂)₂CH₂COCH₂(SO₃Na) CH₂COOCH₂(CF₂CF₂)₂H were used as a surfactant, and also the same actuation as an example 21 was performed, and the emulsion polymerization of FEP was performed.

[0220] The solid content concentration of the FEP latex of obtained this invention was 18.3 mass %, and the number average particle diameter of a primary particle was 205nm. Moreover, when the white polymer obtained by coagulating this latex using a nitric acid was analyzed, it was FEP of HFP11.5 mass % and the melt flow values in 372 degree C and Sg load were 0.0051 ml/sec.

[0221] The experimental result of examples 21-24 was collectively indicated to Table 5.

[0222]

[Table 5]

表 5

例	ラテックス	最新ポリマー		
		固形分濃度(質量%)	一次平均粒子径(nm)	PPVE含有率(質量%)
実施例21	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ COONH ₄	20.5	140	12.3
実施例22	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ COONH ₄	19.5	190	12.1
実施例23	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ COONH ₄	18.8	210	11.7
実施例24	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ COONH ₄	18.3	205	11.5

[0223] Example 25 (emulsion polymerization of PFA)

5000 ppm of CF₃CF₂CF₂CF₂CF₂CF₂COONH₄ were taught to the autoclave with an agitator made from the stainless steel of 6l inner capacity as 3000g of deionized water, and a surfactant. After carrying out the nitrogen purge of the autoclave enough, ethane 20ml (under 25-degree-C atmospheric pressure) was taught as a chain transfer agent under the vacuum, and it stirred by 300rpm and heated to 70 degrees C. Then, perfluoro propyl vinyl ether (PPVE) 45g was added, TFE gas was pressed further fit, and tub internal pressure was set to 0.8MPaG(a). As an initiator, when ammonium persulfate (APS) was prepared so that it might become the concentration of 20 ppm, the polymerization reaction started it, and the fall of a pressure was

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the APS1.0 mass % water solution was prepared with 5.0g plunger pump, and the reaction was started. The reaction was performed at 70 degrees C for 2.5 hours.

[0234] The residual monomer was emitted into atmospheric air after reaction termination, and emulsified liquid was obtained. Moreover, the average rate of polymerization was 32.2 g/hr/liter-water. Some emulsified liquid was taken, with the Microtrac UPA particle-size measuring device made from Honeywell, mean particle diameter was measured and the particle number was computed from the value.

[0235] Examples 30-33 (emulsion polymerization of PVdF)

Except having changed the emulsifier into various kinds, it is making it react like an example 29, and emulsified liquid was obtained, respectively. The result was summarized in Table 7.

[0236] Except having changed example of comparison 1 emulsifier into (CF₂)₂COONH₄, it is making it react like an example 29, and emulsified liquid was obtained. The result was summarized in Table 7.

[0237]

[Table 7]

表 7 : PVdF の乳化重合の実験例と比較例

例	ラテックス	乳剤濃度(質量%)	乳剤濃度(mol/L-水)	重合濃度(g/L-水/時)	粒子径(nm)	粒子数(×10 ¹³ /ml-水)
実施例29	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ COONH ₄	0.25	0.012	47.1	96	194
実施例30	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ COONH ₄	0.25	0.012	31.3	180	17.8
実施例31	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ COONH ₄	0.23	0.012	25.8	253	4.10
実施例32	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ COONH ₄	0.18	0.012	19.2	305	1.08
実施例33	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ COONH ₄	0.25	0.012	23.6	106	48.8
比較例1	CF ₃ CF ₂ COONH ₄	0.25	0.012	32.2	110	55.8

[0238] Example 34 (VdF/HFP copolymerization)

After it taught 45ml of ion exchange water, and 2.8g of emulsifiers to the autoclave made from stainless steel of 100ml content volume and nitrogen permuted with it enough, 4.9g was taught for VdF/HFP mixed gas (40 / 60 mole ratios) by the vacuum. The autoclave was put into the 80-degree C constant temperature bath shaker, and it shook until the pressure was fixed (1.31MPaG). When the pressure became fixed, the APS 0.5 mass % water solution was prepared with 5.0g plunger pump, and the reaction was started. The reaction was performed at 80 degrees C for 0.5 hours.

[0239] The residual monomer was emitted into atmospheric air after reaction termination, and the diameter of a large drop -ized latex was obtained. Moreover, the average rate of polymerization was 104.4 g/hr/liter-water.

[0240] Since the particle diameter of the generated latex particle was small, when it was not able to measure directly, it measured, after carrying out the polymerization of the particle further and enlarging particle diameter. The procedure is explained below.

[0241] After taking a part of generated latex, teaching what was diluted with ion exchange water 10 to 100 times to the autoclave of 100ml content volume and nitrogen's permuting enough, VdF 2.8g was taught by the vacuum.

[0242] The autoclave was put into the 80-degree C constant temperature bath shaker, and it shook until the pressure was fixed (2.40MPaG). When the pressure became fixed, 5.0g preparation reaction was started for the APS 1.0 mass % water solution with the plunger pump. The reaction was performed at 80 degrees C for 0.5 hours.

[0243] The residual monomer was emitted into atmospheric air after reaction termination, and the diameter of a large drop -ized latex was obtained. A part of this is taken and it is Microtrac UPA made from Honeywell. Mean particle diameter was measured with the particle-size

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measuring device, and the particle number was computed from the value.

[0244] Examples 35-38 (VdF/HFP copolymerization)

The latex was obtained by making it react like an example 34 except having changed the emulsifier into various kinds. The result was summarized in Table 8.

[0245] Except having changed example of comparison 2 emulsifier into F(CF₂)₂COONH₄, it is making it react like an example 34, and the latex was obtained, respectively. The result was summarized in Table 8.

[0246]

[Table 8]

表 8: P(VdF/HFP) の乳化剤の異なる例と比較例

	乳化剤	乳化剤 比濃度 (g)	乳化剤濃度 (mol/L-水)	重合温度 (°C-水/油)	粒子径 (nm)	粒子数 (個/L-水)
実施例34	CF ₃ CF ₂ CF ₂ CF ₂ COONH ₄	2.8	0.1	104.1	9.9	1.7×10 ¹⁰
実施例35	CF ₃ CF ₂ CF ₂ CF ₂ COONH ₄	2.3	0.1	85.9	18.0	1.5×10 ¹⁰
実施例36	CF ₃ CF ₂ CF ₂ CF ₂ COONH ₄	2.0	0.1	60.0	30.0	1.2×10 ¹⁰
実施例37	CF ₃ CF ₂ CF ₂ CF ₂ COONH ₄	1.6	0.1	42.9	142.2	7.9×10 ¹⁰
実施例38	CF ₃ CF ₂ CF ₂ CF ₂ COONH ₄	2.2	0.1	30.9	10.1	1.6×10 ¹⁰
比較例 2	F(CF ₂) ₂ COONH ₄	2.2	0.1	74.0	11.9	2.4×10 ¹⁰

[0247] Example 39 (polymerization of a perfluoro elastomer (compulsive emulsification))
To the 5L beaker made from PFA, the emulsifier of 2540g and formula: CF₃CF₂CF₂CF₂COONH₄ for pure water 114g. The perfluoro (alkyl vinyl ether) (PAVE) shown by CF₃CF₂CF₂CF₂COONH₄ CF₂O₂ CF₂CF₂ 2284g, 22.7g and pH regulator (ammonium carbonate) for ICH₂CF₂CF₂ OCF₂CF₂ 12.7g, 3.5g of 1,4-diodoperfluorobutane was put in, it mixed for 60 seconds using the emulsifier (ULTRA-DISPERSER MODEL LX -41 made from Yamato Chemistry), and the reserve emulsified liquid which the volume mean particle diameter of 2 micrometers was made to emulsify was obtained. The volume mean particle diameter at the time of preliminary emulsification was measured using micro truck particle-size-distribution meter HRA9320-X100 by Nihiso Co., Ltd.

[0248] The obtained reserve emulsified liquid was immediately emulsified by emulsification pressure 1000 kgf/cm²G using the compulsive emulsifier (Micro-fluidizer Model M-210 E/H by the micro FURUIDIKUSU international corporation (Microfluidics International Corporation) company), and emulsified liquid was obtained.

[0249] Here, when the volume mean particle diameter of the water-insoluble nature liquid particle in emulsified liquid was measured using micro truck UPA150 particle-size-distribution meter MODEL No.9340 by Nihiso Co., Ltd., volume mean particle diameter was 181nm. Moreover, the particle number per [calculable from volume mean particle diameter and the amount of PAVE contained in emulsified liquid] 1ml of water was 1.65x10¹⁴ pieces, and the amount of emulsifiers per 105 water-insoluble nature liquid particles in emulsified liquid was 2.73x10 to 8 mg, pH in emulsified liquid was 8.9.

[0250] After it put in 4350g of emulsified liquid and 8.8g (hydrate) of ammonium sulfites obtained by the proof-pressure reaction vessel made from stainless steel of 6000ml of content volume and nitrogen gas permeated the building envelope enough, vacuum suction was carried out and carried out to 15 degrees C under stirring, and it pressurized to 4.7 kgf/cm²G by the gas of a fluorine-containing monomer (TFE). When 5.4ml of 0.88 mass % water solutions of a polymerization initiator (APS) was pressed fit, the polymerization reaction started immediately and pressure drawdown happened. When a pressure descended to 3.0 kgf/cm²G, 59g addition preparation of the TFE gas was carried out that the pressure of 3.0 kgf/cm²G should be maintained. After finishing additional preparation, pressure drawdown happened, and 95g addition

preparation of the TFE gas was carried out that the pressure of 2.0 kgf/cm²G should be maintained in the place which carried out pressure drawdown to 2.0 kgf/cm²G. After finishing this additional preparation, pressure drawdown happened, and 98 more addition preparation of the TFE gas was carried out that the pressure of 1.0 kgf/cm²G should be maintained in the place which carried out pressure drawdown to 1.0 kgf/cm²G. After finishing this additional preparation, pressure was discharged, and the polymerization was stopped. In addition, during the polymerization, it pressed 5.4ml of 0.88 mass % water solutions of APS fit at a time every 3 hours. As this result, the aqueous dispersion liquid of a 4849g fluorine-containing polymer were obtained.

[0251] Polymerization time amount was 17 hours and 7 minutes. Moreover, the solid content concentration of the obtained aqueous dispersion liquid was 23.2 mass %, pH was 8.2, and 191nm and the particle number per 1ml of water of the volume mean particle diameter of a fluorine-containing polymer particle were 1.82x10¹⁴ pieces. The fluorine-containing polymer was an elastomer and the presentation (mol % ratio) was TFE/PAVE=77.5/22.5.

[0252] The surfactant of example 40 example 39 — formula: — changing into the compound of H(CF₂CF₂)₂CH₂OCF(CF₃)COONH₄, other conditions were performed similarly and obtained fluorine-containing elastomer.

[0253] The surfactant of example 41 example 39 — formula: — changing into the compound of HANOCO(CF₂CF₂)₂COONH₄, other conditions were performed similarly and obtained fluorine-containing elastomer.

[0254] The surfactant of example 42 example 39 — formula: — changing into the compound of H(CF₂CF₂)₂CH₂OCOC(CH₃)₂CH₂OCF₂CF₂, other conditions were performed similarly and obtained fluorine-containing elastomer.

[0255] The experimental result of examples 39-42 is as in Table 9.

[0256]

[Table 9]

表 9: パーフルオロエラストマーの重合実験例

乳化剤	重合温度 (°C)	重合時間 (分)	重合圧力 (MPa)	粒子径 (nm)	粒子数 (個/mL)	TFE/PAVE (mol %)
実施例 39	CF ₃ CF ₂ CF ₂ CF ₂ COONH ₄	17:07	23.2	1.82×10 ¹⁴	77.5/22.5	
実施例 40	H(CF ₂ CF ₂) ₂ CH ₂ OCF(CF ₃)COONH ₄	20:13	22.8	1.43×10 ¹⁴	78.1/21.9	
実施例 41	HANOCO(CF ₂ CF ₂) ₂ COONH ₄	25:20	22.2	1.33×10 ¹⁴	77.8/22.2	
実施例 42	H(CF ₂ CF ₂) ₂ CH ₂ OCOC(CH ₃) ₂ CH ₂ OCF ₂ CF ₂	18:11	22.9	1.84×10 ¹⁴	79.8/20.2	

[0257] Example 43 (polymerization of fluorine-containing block polymer)

(1) To the autoclave made from SUS316 without the synthetic ignition source of a fluorine-containing polymer of 6l, of content volume 2l, of pure water, a formula: 20g of emulsifiers of CF₃CF₂CF₂CF₂COONH₄ CF₂OCF(CF₃)COONH₄, Stirring by 600rpm, after it teaches 0.18g of disodium hydrogenphosphate and 12 monohydrates as a pH regulator and nitrogen gas fully permeates the inside of a system. The temperature up was carried out to 50 degrees C, and TFE and PMVE were pressed fit, respectively so that internal pressure might be set to 12.0 kgf/cm²G by mole ratios 24/76. Subsequently, 2ml of 188mg [7ml] water solutions of ammonium persulfate (APS) was pressed fit by nitrogen pressure, and the reaction was started.

[0258] The time of falling to 11.0 kgf/cm²G, since the pressure declined with advance of a polymerization reaction — Jo — base — compound KCF₂241 40g was pressed fit, subsequently, TFE was pressed fit in self-*, 20.0g and PMVE22.0g were pressed fit with the plunger pump, and temperature up pressure lowering was repeated.

[0259] 8.4 hours after initiation of a polymerization reaction, when the sum total charge of TFE and PMVE was set to 850g, the autoclave was cooled, the unreacted monomer was emitted, and the aqueous emulsion of solid content concentration 30.0 mass % was obtained.

[0260] This aqueous emulsion was put into the beaker, it was made to freeze in dry ice/methanol, and coagulation was performed, after defrosting, it rinsed, the vacuum drying of

the coagulation object was carried out, and 862g of rubber-like polymers was obtained. Mooney viscosity ML 1+10 (100 degrees C) of this polymer was 80.

[0261] As a result of 19 F-NMR analysis, the polymer presentation of this polymer was TFE81.7 mol %/PMVE38.3 mol %, and the iodine content obtained from elemental analysis was 0.18 mass %. Tg (median) measured with the differential scanning calorimeter (DSC) was -3 degrees C.

[0262] (2) After preparing dispersion by the same actuation as the synthetic above (1) of fluorine-containing block polymer, in the inside of a tub, the permeation back was gone up with pure nitrogen gas, **** was fully gone up to 0.1MPaG(a) (1 kgf/cm²G) by TFE, and 10ml of APS 0.4 mass % water solutions was pressed fit. When it fell to 0.0MPaG (0 kgf/cm²G), recompression was carried out to 0.1MPaG(a) (1 kgf/cm²G) by TFE, since the polymerization reaction started immediately and pressure drawdown happened, when the additional charge of TFE was set to 25g in total and set to 0.1MPaG(a) (1 kgf/cm²G) which are polymerization initiation pressures, pressure was lowered the temperature and discharged and the polymerization was suspended. Polymerization time amount was 2 hours and 30 minutes.

[0263] The solid content concentration of the generated dispersion was 30.6 mass %, the Mooney viscosity of coagulation and the fluorine-containing block polymer obtained by rinsing and drying was ML1+10(100 degrees C)=80, and **** was 891g. The content of a PTFE segment is equivalent to 2.8 mass %.

[0264] The surfactant of example 44 example 43 — formula: — changing into the compound of H(CF₂CF₂)₂CH₂OCF(CF₃)COONH₄, other conditions were performed similarly and obtained fluorine-containing block polymer.

[0265] The surfactant of example 45 example 43 — formula: — changing into the compound of HANOCO(CF₂CF₂)₂COONH₄, other conditions were performed similarly and obtained fluorine-containing block polymer.

[0266] The surfactant of example 46 example 43 — formula: — changing into the compound of H(CF₂CF₂)₂CH₂OCOC(CH₃)₂CH₂OCF₂CF₂, other conditions were performed similarly and obtained fluorine-containing block polymer.

[0267] The experimental result of examples 43-46 is as in Table 10.

[0268]

[Table 10]

表 10: シラフチックブロックポリマーの重合例

乳化剤	重合温度 (°C)	重合時間 (分)	重合圧力 (MPa)	粒子径 (nm)	粒子数 (個/mL)
実施例 43	CF ₃ CF ₂ CF ₂ CF ₂ COONH ₄	81.1/21.9	8.4	80	2.8
実施例 44	H(CF ₂ CF ₂) ₂ CH ₂ OCF(CF ₃)COONH ₄	81.1/21.9	7.5	71	3.4
実施例 45	HANOCO(CF ₂ CF ₂) ₂ COONH ₄	81.1/21.9	7.2	94	3.8
実施例 46	H(CF ₂ CF ₂) ₂ CH ₂ OCOC(CH ₃) ₂ CH ₂ OCF ₂ CF ₂	81.2/21.8	10.0	71	3.5

[0269] Example 47 (seed production of a coating)

After having taught 500ml of deionized water, and 5.0g (number 1) of fluorine system emulsifiers shown in Table 11 to the proof-pressure reaction container with an agitator of 1l, of inner capacity, repeating press fit of nitrogen gas, and degassing and removing dissolved air, the mixed monomer of VdF (74-mol%), TFE (14-mol%), and GTFE (12-mol%) was pressed fit until the internal pressure of this container was set to 1.5MPaG(a) at 60 degrees C. Next, after having prepared 0.2g of ammonium persulfates, having supplied said mixed monomer continuously so that the internal pressure of said container might become fixed by 1.5MPaG(a), and performing a polymerization for 20 hours, the inside of this container was returned to ordinary temperature and ordinary pressure, the polymerization was ended, the aqueous dispersion liquid of the VdF system copolymer of this invention were obtained, and the next trial was performed.

[0270] The trial was performed as follows.

Solid content concentration: said aqueous dispersion liquid were dried at 150 degrees C among the vacuum dryer for 1 hour, and it expressed with the percentage to the mass of the aqueous dispersion liquid before drying the mass after desiccation.

Mean particle diameter: it measured using the laser-light-scattering particle-size measuring device (the product made from Otsuka Electron, trade name ELS-3000). Sedimentation stability: After putting said aqueous dispersion liquid for 60 days at 25 degrees C, it evaluated as follows.

Although the time of change being in a distributed condition was made into O, the particle sedimented and phase separation arose by viewing, the time in which re-distribution is possible was made into **, by the shaking, the particle sedimented further and the time when it could not re-distribute even if phase separation arises and shakes was made into x.

[0271] A result is shown in Table 12.

[0272] In 48 to example 50 example 47, except having adopted the polymerization conditions shown in Table 12, the VdF system copolymer aqueous dispersion liquid of this invention were obtained, and the same trial as an example 47 was performed by the same approach as an example 47. A result is shown in Table 12.

[0273] In example of comparison 3 example 47, except having adopted the polymerization conditions shown in Table 12, VdF system copolymer aqueous dispersion liquid were obtained, and the same trial as an example 47 was performed by the same approach as an example 47. A result is shown in Table 12.

[0274]

[Table 11]

乳化剤	重合温度 (°C)	重合時間 (分)	重合圧力 (MPa)	粒子径 (nm)	粒子数 (個/mL)
1	CF ₃ CF ₂ CF ₂ CF ₂ COONH ₄				
2	H(CF ₂ CF ₂) ₂ CH ₂ OCF(CF ₃)COONH ₄				
3	HANOCO(CF ₂ CF ₂) ₂ COONH ₄				
4	H(CF ₂ CF ₂) ₂ CH ₂ OCOC(CH ₃) ₂ CH ₂ OCF ₂ CF ₂				
5	F(CF ₂) ₂ COONH ₄ (APS)				

[0275]

[Table 12]

乳化剤	重合温度 (°C)	重合時間 (分)	重合圧力 (MPa)	粒子径 (nm)	粒子数 (個/mL)
47	48	49	50	51	52
TFE (mol %)	74	74	74	74	74
TFE (mol %)	14	14	14	14	14
GTFE (mol %)	12	12	12	12	12
重合圧力 (MPa)	1	2	3	4	5
重合時間 (分)	1	1	1	1	1
重合圧力 (MPa)	1.5	1.5	1.5	1.5	1.5
重合時間 (分)	20	22	21	21	22
重合圧力 (MPa)	45.0	44.3	45.2	42.1	44.9
重合時間 (分)	101	113	210	182	136
重合圧力 (MPa)	△	△	△	△	△

[0276] Example 51 (seed polymerization of a coating)

70g of VdF system copolymer aqueous dispersion liquid obtained in the example 47 was taught to the 4 opening flask of 200ml of inner capacity equipped with the impeller, the cooling pipe, and the thermometer, and the special Nonion mold sulfate salt (the product made from Japanese Emulsifier, trade name Newcol 707SF) was added (to this) 1.0% to resin solid content as an